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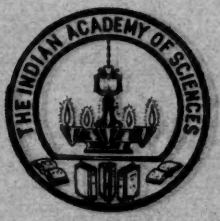

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ELECTROCHEMICAL BEHAVIOUR OF ZINC IN ALKALINE SOLUTIONS

Part I. Constant Current Measurements

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Abstract

The cathodic and anodic polarization of zinc in different concentrations of alkaline solutions has been studied under constant-current conditions. The changes of zinc electrode-potential with reference to a Hg/HgO/KOH system have been measured both in KOH and zincate solutions using a " Luggin " capillary and a specially designed cell, current being drawn from an electronic current stabilizer. Time-potential curves have been plotted and it is found that the anodic zinc passivates at a certain stage showing a sudden rise in potential by as much as 3–4 volts. Before the passivation, the main electrode reaction is the formation of Zn^{++}, while after the passivation it changes to gas evolution. No definite relationship as previously suggested by Muller, between the current density and the passivation time was found, perhaps due to migration and non-linear diffusion effects and other reasons discussed in the paper. It has been found that the behaviour of zinc differs in concentrated alkaline solutions (*i.e.*, 0·5 N to 5 N) from that in dilute solutions (0·2 N to 0·01 N), in which case the open circuit rest-potential of zinc is indefinite and may vary by as much as 500–600 mV., while the maximum passivation jump in potential is about 2 volts only. Also the passivation and the decay of current on breaking the circuit are found to be slower than in the case of concentrated solutions. Colour changes of the zinc electrode, during the polarization, are also briefly described and discussed.

Introduction

In recent times there has been increased interest in the electrochemical behaviour of zinc owing to its potential applications in new types of storage batteries, electrolytic capacitors, semiconductors and rectifiers, etc. Various workers have studied different aspects of the behaviour of zinc in the past;

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but their approach has been rather limited in the sense that they were usually concerned with particular problems of plating and polarization, etc. For example, Morgan and Ralston,[1] Tope,[2] Baroch, Hilliard and Lang,[3] Edward and Swanson,[4] etc., have studied the possibility of depositing zinc from zincate solutions. Abramson,[5] Beklemysheva,[6] Titov and Paleolog[7] and Essin[8] studied the cathodic polarization of zinc on various metals or streaming-mercury electrodes. Similarly, Clark and Akimov,[9] Newbery,[10] Muller,[11] etc., have studied the anodic passivation of zinc, while Huber,[12] Bieri[13] and Laske[14] have been mainly interested in the morphology of the anodic layers produced on zinc. Other workers such as Hoar,[15] Evans,[16] Vernon,[17] Gilbert[18] and Delahay[19] *et al.* have concerned themselves with the corrosion and pitting of zinc. However, a co-ordinated picture of the whole phenomenon does not emerge from these studies. There are also several gaps in the existing information which it is now possible to fill in by the use of new instruments and techniques. It was therefore thought desirable to make a comprehensive and co-ordinated study of the various problems involved in anodic and cathodic polarization of zinc, particularly in alkaline solutions.

EXPERIMENTAL

Apparatus and materials.—The method used was to record the potential changes at the individual electrodes while they were being polarized. The following polarizing and measuring circuits were used:—

Polarizing circuit.—The source of polarizing current was an electronic current stabiliser similar to that described by Thirsk and Wynne-Jones.[20] It employed ten EF 50 valves in parallel and an anode voltage of 500 volts. Its current range could be extended from 60 μA. to about 100 mA. but it was more stable in the range 100 μA. to 40 μA. when a current change of 0·5% required a change of about 300 V across the cell. The current could be set to desired values by means of appropriate resistances in the cathode line of the valves, in series with the cell. Two sets of cathode resistances could be used, either a set of variable resistances or a selected value from a set of fixed resistors.

Measuring circuit.—Three different arrangements to measure the potentials were used depending on the requirements of the measurements, *e.g.*,

(*a*) To obtain the slow changing time-potential curves, a potentiometric circuit with a multi-range Pye Galvanometer was used.

(*b*) To obtain more rapidly changing potentials, a sensitive Cambridge Galvanometer suitably shunted and calibrated was used. As used, it took only about 0·2 μA. per volt deflection of about 40 mm.

(*c*) For very rapid changes an oscilloscopic arrangement could be used to photograph the curves. But it was found that the oscilloscope needed a current of more than 2 μA. per volt deflection and so it was coupled with a suitable single-valve cathode follower which reduced the intake of the current from the experimental cell to about 0·2 μA. only.

Cell.—The electrochemical cell used was of a special design similar to the one recently described by Jones, Lind and Wynne-Jones.[21] It was fitted with a perspex top which held the experimental electrode in such a way as to allow it three independent movements, *i.e.*, vertical, horizontal and rotational. The cathode and anode compartments were fully separated by a joining tube and were about 6″ apart.

Reference electrode.—The Hg/HgO/N-KOH system was used as reference electrode, the actual construction of which was such as to avoid any external bridge while at the same time incorporating a "Luggin" capillary which could be placed quite close to the surface of the experimental electrode. It incorporated a small test-tube with a pin-hole blown in the side to allow electrical contact between the electrode and the main body of electrolyte. The whole assembly could easily go into a side limb of the cell by means of an ungreased ground glass joint. The tip of the capillary was placed in front of the experimental electrode as recommended by Sidney Bernart[22] to give the best current distribution and potential measurement.

Bronsted[23] and Ming Chow[24] have evaluated the E° of the system Hg/HgO (S)-OH′/H_2; Pt at 25° to be about 0·9264 volt. Employing the value of E° = 0·8280 volt for OH′/H_2; Pt half cell, we get Hg/HgO, OH′ E° = 0·0984.

Solutions.—All solutions were made from "Analar" KOH and ZnO in distilled water and were stored in 'Pyrex' vessels, fitted with a U-tube containing "Sofnolite" to absorb CO_2. Solutions could be taken out by pumping air through these "Sofnolite" tubes.

The electrolyte in the cell was changed every day and care was taken to see that the concentration of zincate ion did not materially change during the course of the experiment. However, during the experiment the solution was accessible to air and not stirred.

Zinc.—Two types of zinc were used:—

(i) Containing 0·2% of Pb and 0·05% of Cd.

(ii) 99·99% pure zinc.

Temperature.—A thermostat maintained at 25° C. (± 0·1° C.) was used during all measurements of potential changes. Platinum foil was used as the auxiliary electrode.

Experimental technique.—It was decided, after some preliminary experiments, that pure zinc sheet electrodes of 99·99% purity would be the most convenient to use. The electrodes consisted of $1 \times 1 \times 0{\cdot}3$ cm.^{3} sheets, to the centre of one face of which a thick steel wire was firmly but carefully soldered so as not to affect the zinc as far as possible.

Preparation of electrode surface.—Factors affecting the choice and selection of electrode materials and of the methods of prepolarization-preparation and cleaning have been well discussed by Briggs.[25] Clearly, the question of pretreatment of electrodes is very complex and complicated and no clear picture of all its effects is so far available. Some of the confusion and diversity of experimental data reported by various workers in the past might easily have been due to the different pretreatment techniques employed. The procedure adopted finally was to smooth out the flat face of the zinc electrode by rubbing down with six grades of " SIA " emery paper (from 0 to 6/0) lubricated with alcohol, and rotating the face by 90° between successive grades. A final treatment of rubbing with " diamentine powder " was tried but found to be unsatisfactory as diamentine tended to get embedded in the surface. The electrodes were, therefore, given a final rub first with plain parchment paper and then with ' Selvyt ' cloth lubricated with alcohol, before being put in the cell.

TABLE I

Cathodic polarization

Room temperature . Potentials *vs.* Hg/HgO/N—KOH reference electrode in volts.

Concentration of KOH	Initial Rest Potential	c.d. mA./cm.^{2}	Potential after 1 minute of start of current	After 10 minutes
N	−1·35	0·1	−1·37	−1·38
		14·0	−1·60	−1·66
		40·0	−2·00	−2·03
N/100	−0·5	0·1	−1·2	−1·15
2·5 N	−1·36	20·0	−1·38	−1·41
N	−1·32	20·0	−1·5	−1·56
N/2	−1·28	0·5	−1·34	..
N/5	Variable	1·0	−1·28	−1·30
N/10	−0·6 to	2·0	−1·20	−1·30
Saturated with ZnO	−1·2	0·2	..	−1·1

Stopping off.—The rest of the electrode and the wire-lead were given two coats of either the commercial stopping-off compound "Lacomit" or a polystyrene cement.

Polarization procedure.—Two minutes after the electrodes were introduced into the cell, their potential with respect to the reference electrode was measured. By careful working and use of the above technique the reproducibility of this could be achieved within $\pm$ 5 millivolts. Only when this was achieved was the constant current from the stabilizer switched on and the polarization started. All current densities were estimated on the apparent area of the electrode surface.

In the following experiments, the solutions were not stirred.

Results

(*Note.*—All potentials as given in this section are with respect to Hg/HgO/N KOH half-cell.)

Cathodic polarization

In 2·5 N—KOH saturated with ZnO.—on cathodic polarization, zinc deposits could easily be obtained from such solutions. At 20 mA./cm.^{2} the initial potential of about $-1\cdot36$ V. slowly became more negative by about 0·1 V. in half an hour, as the deposition proceeded.

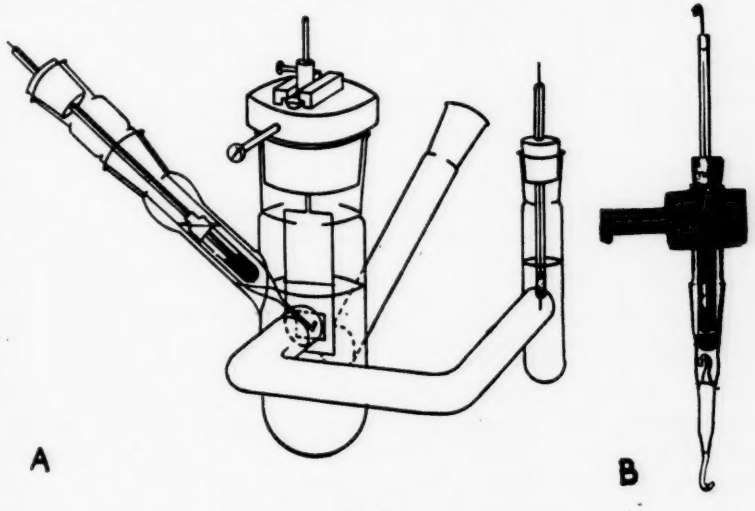

Fig. 1.

In N-KOH saturated with ZnO.—Zinc deposits at 20 mA./cm.^{2}, the potential changing quickly at first from about $-1\cdot3$ to $-1\cdot5$ V. in 30 seconds, and then gradually becoming more negative by 50–60 mV. in 5 minutes or so.

In N-KOH.—The steady initial potential (without polarization) of zinc electrode was about $-1\cdot35$ V. On commencing the polarization at a c.d. of 14 mA./cm.^{2} the potential first jumped to about $-1\cdot58$ V. and then gradually decreased to $-1\cdot66$ in about 15 minutes. On switching off, the recovery was very rapid up to $-1\cdot36$ V. followed by a slow rise to $-1\cdot35$ V. in about 15 minutes. Working with the same electrode and varying the current density in the range 100 μA. to 40 mA./cm.^{2} and allowing time for the potential to become sufficiently steady, it was found that the potentials obtained in the increasing and decreasing order of current densities were very similar but it was easier and quicker to achieve steady values of potential in the decreasing order than in the increasing order of current densities.

The potential of the zinc electrode varied from $-1\cdot37$ to $-2\cdot03$ V. when the current density was varied from 100 μA. to 40 mA./cm.^{2} On plotting the potential against the logarithm of the current density from the above preliminary results, all the points between current density 40 mA. to 500 μA./cm.^{2} were found to lie on a straight line. Only the points corresponding to lower current densities were on a curve convex to the "log i" axis.

In $1\cdot65N$*-KOH* + 4 *gm./lit. of ZnO.*—The potential changes corresponding to cathodic polarization at various current densities are shown graphically in Fig. 2.

As shown there, the zinc electrode potential was found to oscillate at current densities of the order 10–20 mA./cm.^{2} Also, on switching off the current the recovery of potential was very rapid.

The potential values corresponding to cathodic polarization at other current densities in some solutions are tabulated in Table I.

Anodic polarization

In $1\cdot65N$*-KOH containing* 4 *gm./lit. of ZnO.*—The potential changes at various current densities are shown graphically in Fig. 2.

The upper part of the diagram represents conditions of anodic polarization, while the lower part represents conditions of cathodic polarization. Each curve shows the potential changes at a particular value of the current density and where the potential change was too rapid to be followed accurately by the measuring arrangements (*a*) and (*b*) as described earlier, a broken

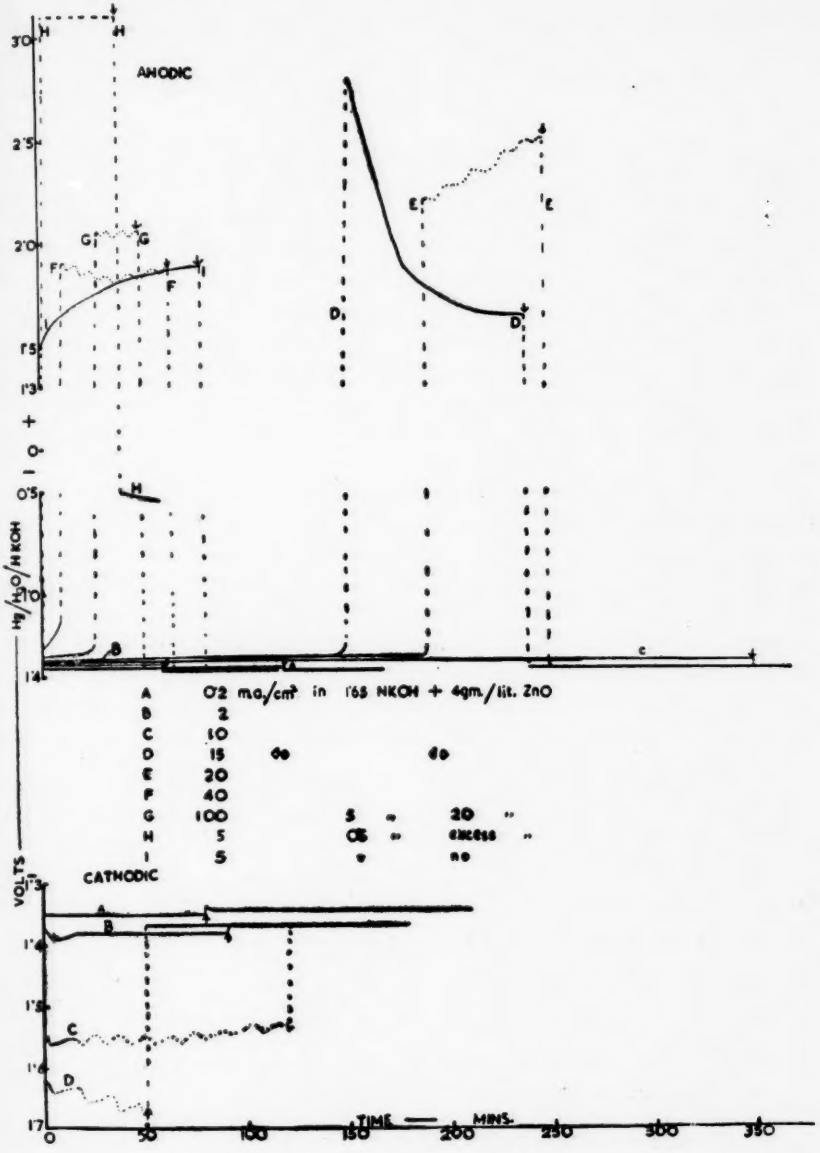

FIG. 2. Potential—Time Curves for Zn in Alkaline Solutions.

line is shown on the curve. When the current was switched off the potential changed rapidly and this decay is indicated in each curve by an arrow pointing downwards on the anodic and upwards on the cathodic polarization curves.

At current densities higher than 10 mA./cm.^{2} the zinc electrode seems to be clearly characterized by a well-defined passivation stage, when the potential may suddenly jump as much as 4 volts or so depending on the conditions of polarization. At current densities of the order of 15–20 mA./cm.^{2} the passivation may occur at any time between 2½ and 4 hours of polarization. Within this range the actual passivation time was not found to be reproducible. At 40 mA./cm.^{2} the passivation may set in within 10–15 minutes of polarization while the maximum potential reached may only be about + 1·9 V. The relation between the current density and the time taken for passivation under these conditions was not found to be a simple or definite one. The potential of the passive electrodes may vary from + 1·85 to + 2·7 V. and is not exactly reproducible, although it obviously depends on the current density to some extent and approximately lies in the same region under similar conditions. At 20 and 40 mA./cm.^{2} the zinc electrode potential was found to oscillate and fluctuate with time, although it is difficult to say how far this phenomenon was truly periodic in nature, as the matter was not investigated in detail. However, it may be of some interest to note that Schwabe[26] quite recently published his study of true periodic phenomena on zinc electrodes in chloride, sulphate, nitrate and perchlorate solutions. The decay of potential on switching off the current was very rapid in all these cases.

In 5 N-KOH containing 20 gm./lit. ZnO.—No passivation occurs even after 5 hours and at a current density of 50 mA./cm.^{2} while at 100 mA./cm.^{2} partial passivation occurs in about 30 minutes or so, when an electro-polishing effect is obtained at a slightly fluctuating potential of about + 2·05 V. Decay of potential on switching off the current is rapid in these cases also.

In 2·5 N-KOH saturated with ZnO.—Zinc does not passivate when polarised at current densities lower than 40 mA./cm.^{2} Even at 40 mA./cm.^{2} it freely goes into solution with an overvoltage as low as about 50 mV. and is not found to passivate upto 3 hours. However, above 55 mA./cm.^{2} passivation is found to occur in about 40–60 minutes when the potential suddenly rises to about + 2·3 V.

In N-KOH saturated with ZnO.—At 10 mA./cm.^{2} it takes about 2-3 hours before zinc passivates suddenly and the potential rises from the initial value of about − 1·3 to + 2·4 V. However, within a few minutes the potential

falls again slightly and then becomes steady at about + 2·0 V. At 20 mA./cm.^{2} the potential first slowly rises to about − 1·15 V. in 18–20 minutes when it suddenly passivates and the potential jumps to + 2·0 V. At 40 mA./cm.^{2} the passivation is almost immediate.

If after passivation, the current is switched off and the decay followed, it is found that the potential very rapidly falls from + 2·0 V. to about 0 V. and then gradually falls to about − 0·7 V. in 3 minutes or so when it either becomes steady, or further falls towards the equilibrium potential depending on the history of polarization.

In N-KOH solutions the pre-polarization rest potential is − 1·34 to − 1·35 V. When an anodic current of 14 mA./cm.^{2} is switched on it jumps to − 1·28 V. and then slowly rises to − 1·24 V. in about 15 minutes. On switching off, the decay is very rapid and the electrode almost regains its rest potential.

In 0·5 *N-KOH.*—A 2 mA./cm.^{2} the potential varies only slightly (about 50 mV.) in 4–5 hours, when there is sudden passivation and the potential jumps to about + 2·0 V. and then changes little. However, at 5 mA./cm.^{2} the passivation is gradual and sets in within a few minutes as shown in Fig. 2. During this time a thin greyish film is formed on zinc which slowly turns into a dark blue anodic layer. This layer can be peeled off by making the electrode cathodic for a few minutes at a current density of about 200 μA.

In 0·5 *N-KOH saturated with ZnO.*—No passivation occurs within 20-30 minutes at 2 mA./cm.^{2}, but if the current density is then raised to 5 mA./cm.^{2} passivation quickly sets in and the potential jumps to somewhere in the region of + 2·5 V. or more depending on the nature and time of previous treatment of the electrode. However this jump is not very reproducible. Also, the decay of the potential, when the current is switched off after the passivation, is not immediate but gradual and there is an arrest in the potential region of − 0·5 V.

In more dilute solutions.—Time potential curves for some more dilute solutions are shown in Fig. 3. The decay of potentials, on switching off, is also shown. A few main potential values at some polarization stages are also given in Table II.

In all solutions, with or without ZnO, of concentration 0·2 N-KOH or lower, the equilibrium rest potential of an unpolarized electrode is often found to lie in the region of − 0·5 V., although it may vary and in some cases even tend towards − 1·2 V., depending on the conditions of the electrode surface, amount of oxide formed or present and the dynamics of corrosion

TABLE II

Anodic polarization

Room temperature . Potentials *vs.* Hg/HgO/N—KOH electrode in volts.

Concentration of KOH	Initial Rest Potential	c.d. mA./cm.^{2}	Passivation Time	Potential		Remarks
				Before Passivation	After	
N	−1·35	14·0		−1·24		Does not passivate for several hours
N/2	−1·3	5·0	About 5 minutes		+1·5	Potential continues to rise slowly and reaches +1·85 V. in 60 minutes
		2·0	4·5 hours	−1·3	+2·0	
N/10	Variable	2·0	About 5 minutes	Variable	+1·4	Gradual passivation
	−1·2 to −0·5	0·1		−1·1 to −0·5	+1·7	
2·5-N	−1·36	10·0		−1·34		No passivation even in 3 hours
		40·0		−1·32		
		55·0	50–60 minutes	−1·25	+2·2	
N	−1·32	10·0	2·5–3 hours		+2·4	
		20·0	18–20 minutes	−1·15	+2·0	
		40·0	immediate			
N/2	−1·32	5·0	0–1 minutes		+2·8	
		50·0	immediate		Above +2·8	
N/5	Variable	2·2	1–5 minutes	Slowly rises	+1·4	Gradual passivation
N/10	−1·2 to −0·6	1·0	0–5 minutes		+1·7	

Saturated with ZnO

taking place. The passivation at current densities 2 mA./cm.^{2} and lower, is gradual and can often be followed through all its stages. It may take 1–5 minutes to passivate completely and reach a peak voltage of about +1·5 V. Similarly, the decay is also gradual and there is a potential arrest in the region of − 0·5 V.

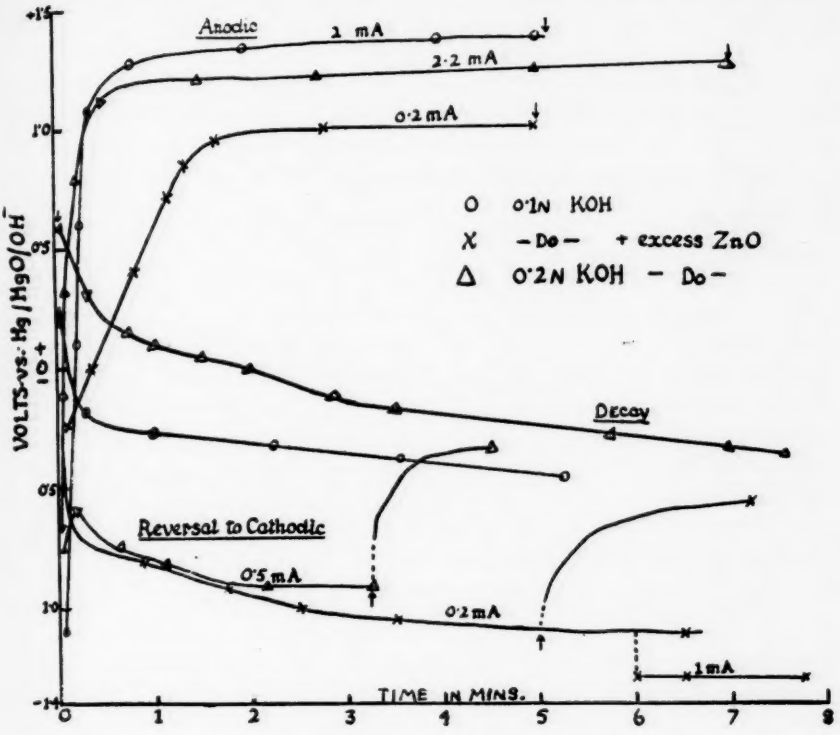

FIG. 3. Polarisation Curves for Zn.

GENERAL OBSERVATIONS

(*a*) In dilute solutions, if a good anodic passive layer has initially been formed by polarizing at 5 mA./cm.^{2} or higher for some time and then the current is reduced, the potential falls only slightly at first but the electrode may become active again if left for a long time and if the current density is very low.

(*b*) However, if the current is reversed and made cathodic at 50–100 μA./cm.^{2}, after passivation, a significant amount of coulombic capacity can be observed for a time comparable to the anodic polarization time, before the potential reaches the $-1{\cdot}0$ V. mark. Then on switching off the cathodic current, the potential tends to rise again and may reach a value of up to $-0{\cdot}5$ V. This shows that under these conditions, it might be possible to

carry out, to a certain extent, some electrochemical oxidation or reduction entailing one of the following processes:—

(i) oxidation and reduction of zinc oxide layers ;
(ii) deposition and dissolution of zinc ;
(iii) growth and dissolution of anodic layers ;
(iv) evolution of oxygen or hydrogen.

It would be of great interest and practical importance from the alkaline accumulator view-point if the first of the above processes could be carried out electrochemically. However, our later experiments (under publication) tend to show that the first process is not very easy and is, in any case, improbable between $-0{\cdot}5$ V. and $1{\cdot}0$ V. Similarly the second process has also been shown to be inefficient and is improbable under these conditions so that finally a choice between the third and the fourth processes is left. It is very difficult to prove or disprove either of these two conclusively with the data available at the moment. However, constant overvoltage experiments do indicate that in cathodic reduction under the above conditions, most probably hydrogen is evolved on the zinc oxide surface which covers the electrodes in the potential regions of $-0{\cdot}5$ V., in dilute solutions.

However, another disadvantage from the accumulator view-point is that the potential is not very constant and that there is no definite arrest. On the one hand, under passive conditions the anodic potential may wander between $+1{\cdot}5$ V. and $+2{\cdot}8$ V. depending on the concentration and current density, and on the other, under cathodic polarization it drops suddenly to $-1{\cdot}3$ V. or lower in concentrated solutions, when zinc may be deposited or hydrogen evolved depending on the availability or otherwise of zincate ions. In dilute solutions, although the potential variation is not so large, the tendency for gas evolution on the Zn/ZnO/KOH surface also becomes more pronounced and oxygen may be given off below $+1{\cdot}5$ V. while hydrogen evolution starts between $-0{\cdot}5$ V. and $1{\cdot}0$ V. Thus, although apparently the decay of potential is slow, in reality it does not involve any electrochemical reduction of the zinc oxide electrode.

(*c*) In all solutions if after passivation, the current density is gradually reduced the potential of the electrode gradually falls till either with increasing time or falling current density it ultimately becomes active again. However once passivated, the electrode potential does not fall back to the active region as soon as the current density is reduced below 20 mA./cm.^{2}, as suggested by Newbery.[10] There is a time lag depending on the previous history and conditions of the polarization of the electrode.

(*d*) A very large variety of anodic layers of different colours and appearance may be formed on zinc in alkaline solutions. The main influencing factors seem to be (i) current density, (ii) concentration of electrolyte, (iii) composition of electrolyte, *i.e.*, presence of zincate, etc., (iv) nature of electrode surface and purity of material and (v) duration of polarization. It seems that factors (ii) and (iii) exert their influence mainly by the variation of the dissolving effect of the electrolyte on the anodic layers, *e.g.*, layers are darker when the solutions are concentrated or no zincate is present than in weaker or zincate solutions. This is presumably due to the formation of excess interstitial zinc ions in the layers which are thereby rendered dark, when the solution exerts a significant dissolving effect.

However no detailed study of the colour and morphology of these layers was made in our experiments as Huber and his co-workers[12] have already investigated this aspect.

Discussion of Passivation Curves in Concentrated Solutions

Various reasons for sudden passivation have already been discussed by Muller.[11] In addition the following may also be considered :—

(*a*) Phase changes on the surface which may involve sudden changes in the internal potential drops between metal/oxide, oxide/solution and across the oxide layer.

(*b*) Change in mode of conduction, *i.e.*, from ionic to electronic (through interstitial ions, etc.) leading to change in the nature of reaction on the electrode.

It is difficult to decide and specify how far and which one of the above possibilities applies to a particular case. It is now realized that, in fact, measurements based on constant current methods alone are probably not sufficient to conclusively differentiate between the above. It is felt that in the case of constant current methods all the various stages of gradual polarisation and passivation may not be observed due to the artificial necessity of forcing a predetermined current through the electrode. For example, observations on a fixed current density could only show those points of a potential current curve which lie on the co-ordinates of the current density being forced through. Such observations would therefore essentially be discontinuous. This may also be the reason why the potential after passivation wanders over such a wide range, *i.e.*, $+1{\cdot}5$ to $+2{\cdot}8$ V., even though the basic reaction is the same, *i.e.*, gas evolution. Thus, these passivation potentials only indicate the potential at which a particular current density can be sustained under the experimental conditions.

The slight gradual fall of potential after the initial passivation jump has been observed in some other cases also. Efforts have been made to explain this on the basis of:

(*a*) Recrystallisation or phase changes on the electrode surface.

(*b*) Breakdown of one dielectric and the establishment and stabilisation of another.

(*c*) Phenomena of nucleation and nucleus growth.

(*d*) Changes in the dissolving power of the electrolyte in contact with the anodic layer.

Hunter *et al.*,[27] have shown that in the case of porous anodic layers in general and for aluminium oxides in particular, the temperature and concentration of the electrolyte in the pores are very different from those of the bulk. If the case of zinc is taken to be similar, it may be assumed that when the resistance suddenly changes thereby causing the potential to jump, within a few seconds the heat produced in the pores and on the oxide-solution interface increases the solubility of the oxides slightly thereby reducing the layer thickness and allowing the potential to fall accordingly till a new equilibrium is established.

Passivation time.—Considerable efforts[13, 28] have been made to establish a relation between passivation time and current density, etc. But, it appears that there are many more variables involved than appear superficially or have so far been taken into account. For example, as not much attention was paid in the past to the pre-polarization preparation and surface conditions of the electrode, the results of various workers cannot be properly co-related and co-ordinated. Moreover, recent efforts to verify Muller's equation have taken into consideration only short passivation times of the order of a few seconds at high current densities. It is therefore not surprising that under the conditions of our study we did not find passivation times to be reproducible presumably due to the convection and non-linear diffusion effects interfering. This was perhaps the case in Bieri's[13] experiments as well.

DISCUSSION OF RESULTS IN DILUTE SOLUTIONS

In dilute or saturated zincate solutions the time-potential curves obtained are significantly different from those in concentrated alkaline solution, the main reason probably being that the dissolution rate of anodic layers is much larger in concentrated solutions. Saturation with zincate reduces the dissolving power but can by no means stop it completely as it has been

shown that even such saturated solutions can always take up more zinc which goes in as a complex and is then slowly precipitated out. The solubility may also be enhanced by the local increase of pH at the anode due to migration of OH' ions.

But obviously the complex ion formation is much slower in dilute KOH and saturated zincate solutions thereby encouraging other reactions, *e.g.*, layer formation and growth and ultimately passivation and gas evolution to compete more favourably.

Thus, in the interpretation and discussion of time-potential curves in dilute solutions, the only significant point is that the pre-polarization or post-polarization rest potential tends to stay in the region of $-0{\cdot}5$ V. and that even if a cathodic current of $100\,\mu$A./cm.^{2} is passed the potential does not drop below $-1{\cdot}0$ V. Now we know that the hydrogen discharge or reduction potential of zinc oxide on zinc surface is mostly below $-1{\cdot}3$ V. So either of these processes are not very probable if the surface of the electrode is metallic zinc. But there is reason to believe that zinc is often covered with a very thin oxide film (Raether,[29] Huber,[12] Bieri,[13] Laske,[14] etc.) which may be dissolved by concentrated solutions but remains more or less unaffected in dilute solutions. So the potential that is being measured in dilute solutions is not Zn/electrolyte but Zn/ZnO/electrolyte potential. It is on the surface of this thin, adherent, covering layer of oxides, that both zinc deposition from zincate solutions, and hydrogen evolutions from pure alkali solutions can take place. Between $-0{\cdot}5$ and $-1{\cdot}2$ V., it appears that only hydrogen evolves, the rate and the potential depending on the current density used.

Clark and Akomov[9] have also observed that the open circuit potential tends to become slightly more positive with time. The reason why we find only a pseudo arrest with a varying potential range and not a particular fixed potential value corresponding to Zn/ZnO/KOH may be that in open circuit the potential tends to accommodate itself according to the corrosion balance in which H_2 evolution rate = zinc corrosion rate and the electrons produced in the reaction

$$Zn \longrightarrow Zn^{++} + 2e$$

are exactly equal to those used up in

$$2H^+ + 2e \longrightarrow H_2.$$

Our constant potential results tend to confirm the above explanation and conclusively show that hydrogen can be deposited on ZnO at potentials + ve

to the equilibrium rest potentials. These observations are in conformity with those reported by Vermilyea[30] in the case of tantalum.

ACKNOWLEDGEMENT

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VERTICAL SOUNDINGS AT AHMEDABAD DURING PARTIAL SOLAR ECLIPSE ON 14th DECEMBER 1955

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Abstract

The results of vertical ionospheric soundings at Ahmedabad during the partial (magnitude 47%) solar eclipse on 14th December 1955 are discussed. The critical frequency of the E layer on control days varied according to the law $f_0E = k \cos^n \chi$, k and n having the mean values 4·06 Mc./s. and 0·37 respectively. The variation of f_0E during eclipse period was roughly consistent with that of Chapman Layer with a recombination coefficient of about $0{\cdot}8 \times 10^{-8}$ cm.^{3} sec.$^{-1}$ The critical frequencies of E_1, E_2 and F_1 layers decreased during eclipse, though the variations were irregular. The percentage deviation of f_0F_2 on the eclipse day from the control day values showed a minimum at about the middle of the eclipse period. There were indications of the formation of $f_{1\cdot5}$ during the latter part of the eclipse. Semi-thickness of the F_2 layer had increased during the eclipse period. Sporadic E layer was not affected by the eclipse.

The present article describes the results of vertical ionospheric soundings made at Ahmedabad during the partial solar eclipse of 14th December 1955.

The times of the various phases of the ground eclipse are given in Table I.

Table I

	Time 75° E.M.T.	Solar altitude
Commencement of the eclipse ..	1014 hours	37°
Maximum phase of the eclipse ..	1210 ,,	44°
End of the eclipse ..	1400 ,,	37°
Magnitude of the eclipse ..	47%	..

As the eclipse occurred almost at noon, there was very little difference in the time of the phases of the eclipse at ground and at ionospheric levels, and so no detailed calculations of these latter times were made. The portion (p) of the solar disc unobscured by the moon, the cosine of solar zenith angle ($\cos \chi$), and the product ($p \cdot \cos \chi$) during the eclipse are shown in Figs. 1 (a) and 1 (b). $p \cdot \cos \chi$ varied from 0·6 at the beginning and end of the eclipse to 0·37 at the maximum phase of the eclipse.

The British N.P.L. type ionospheric recorder of the Physical Research Laboratory was used for all the measurements. The equipment covered 0·65–15·4 Mc./s. in four minutes; the frequency range 15·4–25 Mc./s. was not used. On the control days, P′-f records were taken at intervals of fifteen minutes each day from 09 hr. to 15 hr. On the eclipse day, records were taken every five minutes from 10 hr. to 14 hr. The variation of critical fre-

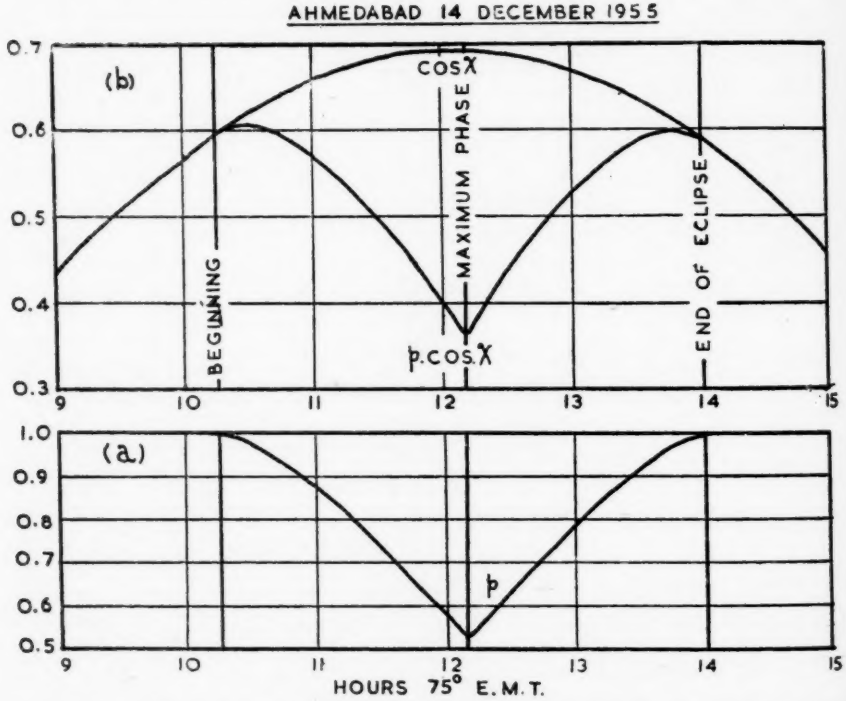

FIG. 1. (a) The variation of fraction (p) of the solar disc unobscured by the moon during the solar eclipse of 14th December 1955 at Ahmedabad. (b) The variation of the cosine of solar zenith angle ($\cos \chi$) and the product $p \cdot \cos \chi$ during the solar eclipse of 14th December 1955 at Ahmedabad.

quencies and the minimum virtual heights of E, E_1, E_2 and F_1 layers on control days and on the eclipse day are shown in Fig. 2. Figure 3 shows the critical frequencies (f_oF_2), the minimum virtual heights ($h'F_2$) and the virtual heights at $0{\cdot}83 \times f_oF_2$ (h_pF_2) on the eclipse day and on the control days.

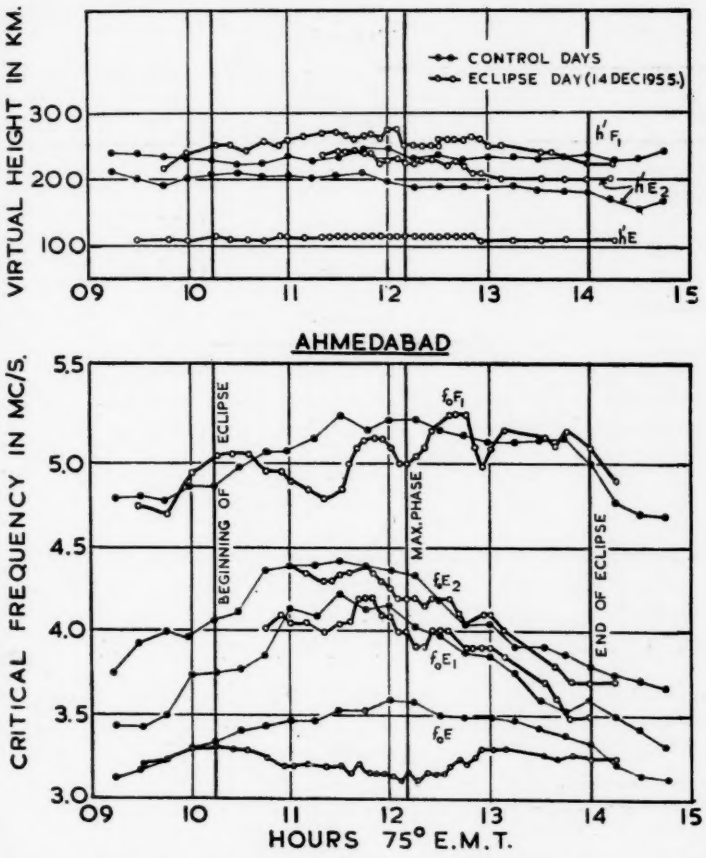

FIG. 2. The variation of critical frequencies and virtual heights of E, E_1, E_2 and F_1 layers on control days and on the eclipse day.

E layer.—As expected, the E layer critical frequencies decreased from the start of the eclipse and remained lower than the normal-day values during the entire period of the eclipse. The dip in f_oE during the eclipse was flat, as the eclipse occurred at noon and was only partial. The minimum virtual height of E did not show any change during the eclipse. The critical

frequencies of the E layer on different control days are plotted against the corresponding values of $\cos\chi$ on double logarithmic paper in Fig. 4. The straight line nature of the curve joining the points indicated that f_0E varied with solar zenith distance according to the relation $f_0E = k\cos^n\chi$. The values of k and n on the control days are given in Table II.

TABLE II

December 1955	kE	nE
11	4·10	0·42
12	4·00	0·38
13	4·10	0·33
16	4·05	0·35
Mean ..	4·06	0·37

Ratcliffe (1956) has shown that during a solar eclipse

$$\frac{N_1^2}{N_0^2} = \frac{S_1\cos\chi_1}{S_0\cos\chi_0},$$

where N is the maximum electron density, S is the flux of ionising radiation, χ is the solar zenith angle and the subscripts 1 and 0 refer *to the times when the ionisation is not changing with time.* We find that for the E layer, N_1^2/N_0^2 was equal to 1·27 whereas $S_1\cos\chi_1/S_0\cos\chi_0$ equalled 1·67.

Appleton (1953) has shown that the recombination coefficient in the E region can be determined from the time delay τ of the maximum of f_0E behind noon according to the equation

$$\tau = \frac{1}{2\alpha N}.$$

Using the above equation the value of α E was found to be $0{\cdot}78\times10^{-8}$ cm.^{3} sec.$^{-1}$ In Fig. 5 the variation of maximum electron density in E layer observed on control days and on the eclipse day are compared with the theoretical variations calculated for the period of the eclipse with assumed values of $\alpha = 0{\cdot}75\times10^{-8}$ and $0{\cdot}8\times10^{-8}$ cm.^{3} sec.$^{-1}$ Neither of the theoretical curves satisfied the observed points. The observed values were lower than the theoretical values during the first half of the eclipse, while they were higher

during the latter half of the eclipse. Similar early falls of $_{,0}$E have been observed by other workers (Pierce, 1948; Minnis, 1955; Szendrei and McElhinny, 1956). This asymmetry has been attributed to the non-uniform distribution of the sources of ionising radiation on the solar disc.

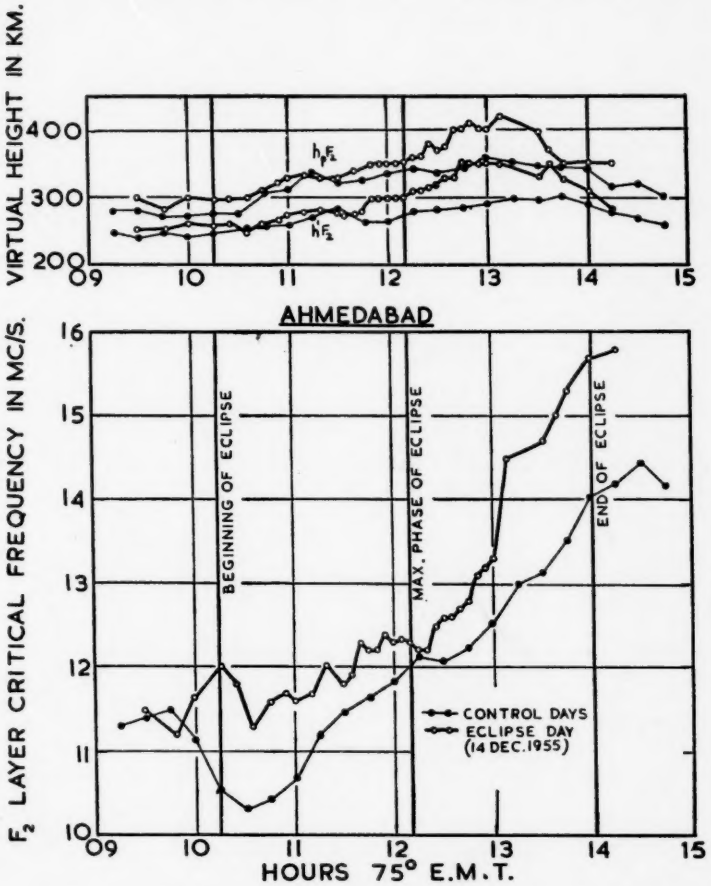

FIG. 3. The variation of critical frequency (f_0F_2), minimum virtual height ($h'F_2$) and virtual height at $0{\cdot}834 \times f_0F_2$ (h_pF_2) of the F_2 layer on control days and on the eclipse day.

E_1 and E_2 layers.—Besides the normal E layer two more intermediate layers, called E_1 and E_2, are regularly observed at Ahmedabad (Rastogi, 1954; 1956). The eclipse occurred at the time when E_1 and E_2 layers were being

formed out of the ledge in F_1 layer. The effect of the eclipse was not so clear on E_1 and E_2 as on E.*

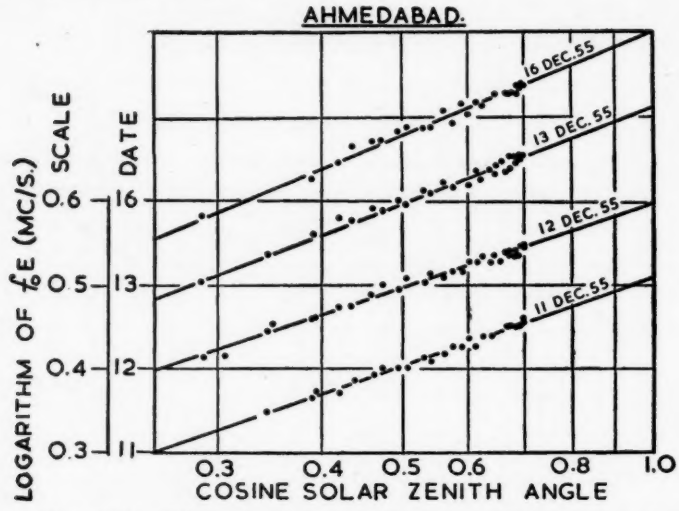

FIG. 4. The variation of the critical frequency of the E layer with the zenith angle of the sun.

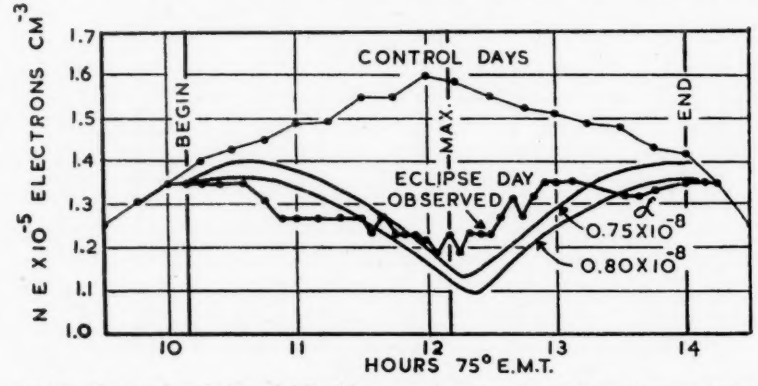

FIG. 5. Expected variation of f_0E with assumed values of α and the observed variation on the eclipse day.

F_1 layer.—It is known that at most places, the F_1 layer is not quite clear during winter months and during times of high solar activity. At high lati-

* A decrease of E_2 layer ionisation during a solar eclipse was more clearly seen during another eclipse observed at Ahmedabad, *viz.*, on 20th June 1955, as shown in Fig. 6. Decreases of E_2 ionisation during solar eclipses have been observed by other workers Schafer and Goodall (1935), Estrabaud (1953), Szedenrei and McElhinny (1956), Bibl and Delobeau (1956).

tudes it is observed only in the summer months in the middle of the day. At Ahmedabad the F_1 layer was most defined during summer and in the period of low sunspot activity. In December 1955, solar activity had increased considerably and the F_1 layer was not very clear. On the control days, the

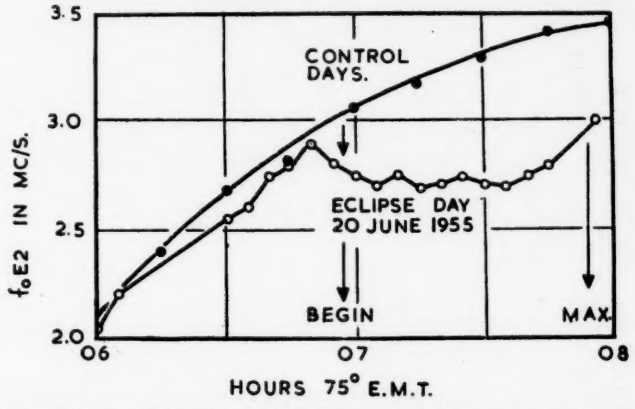

FIG. 6. The variation of f_0E_2 during the eclipse on 20th June 1955 at Ahmedabad.

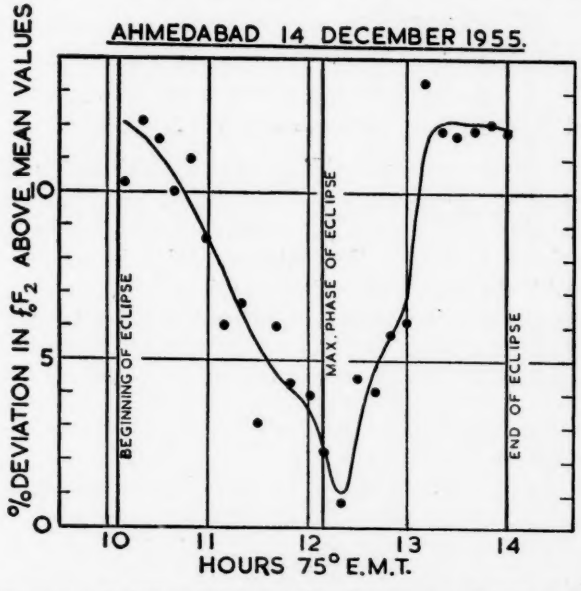

FIG. 7. Percentage deviation of F_2 layer critical frequency on the eclipse day above the control day values.

F_1 layer never gave a sharp cusp on P'-*f* records and its presence could be detected on the P'-*f* traces only by a flat cusp. The f_0F_1 values given are the frequencies at the point of inflexion in the P'-*f* trace and do not represent the maximum electron density in the F_1 layer.

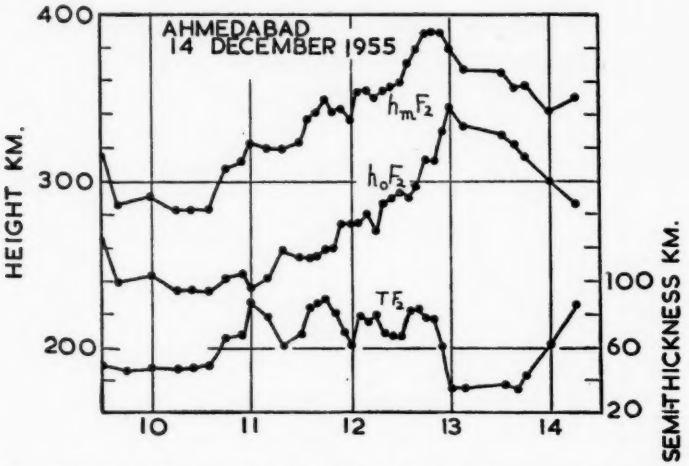

FIG. 8. Variation of the height of the base (h_oF_2) height of maximum ionisation (h_mF_2) and semi-thickness of the F_2 layer during the eclipse.

The f_0F_1 values during the eclipse showed a decrease but the data cannot be considered to be on par with those of the E layer.

F_2 layer.—On the eclipse day, f_0F_2 values were higher than those on the control days, during the entire period of the eclipse. The deviation of f_0F_2 on the eclipse day above the control day values was minimum at the middle of the eclipse as shown in Fig. 7. On control days f_0F_2 increased steadily from 10–14 hours with the same rate. On the eclipse day, the rate of increase of f_0F_2 during the first half of the eclipse was smaller than that on normal days, while after the maximum of the eclipse, f_0F_2 increased more rapidly than on normal days.

The minimum virtual height ($h'F_2$) and the virtual height at $0{\cdot}834 \times f_0F_2$ (h_pF_2) on the eclipse day were not very different from those on control days till about 1130 hours. After 1130 hours both $h'F_2$ and h_pF_2 increased above the control day values and reached the maximum at about 13 hours, after which they returned to normal at about 14 hours. The values of the semi-thickness (TF_2), the height of base (h_oF_2) and the height of maximum electron density h_mF_2 of the F_2 layer were determined by Booker and Seaton's method

(1940). The variations of these quantities during the eclipse period are shown in Fig. 8. The changes in the maximum electron density (N_mF_2) and the total electron content in a unit vertical column upto h_mF_2 ($nF_2 = 2/3\ T\ N_m^2$) are shown in Fig. 9. h_mF_2 increased shortly after the beginning of the eclipse,

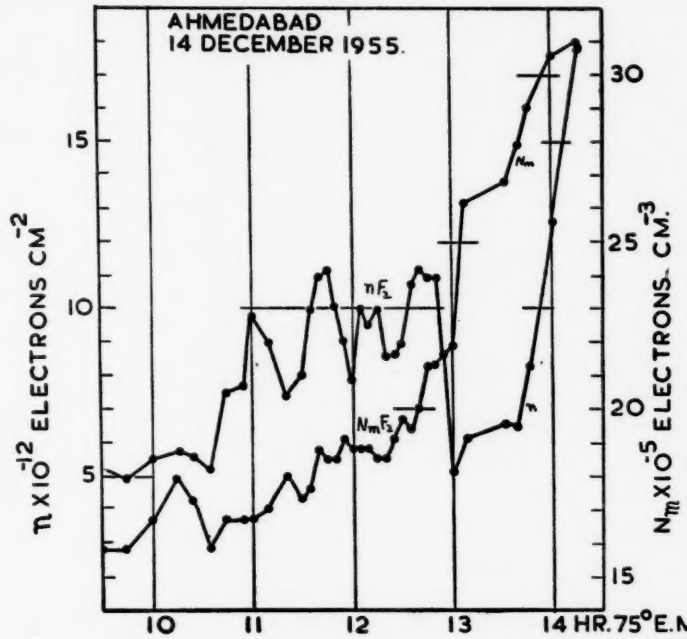

FIG. 9. Variation of the maximum electron density ($N_m F_2$) and total electron content (nF_2) of the F_2 layer during the eclipse.

reached a maximum about an hour after the maximum phase of the eclipse and dropped to its normal value after the end of the eclipse. h_0F_2 also increased similarly and reached a value as high as 340 km. at 13 hours. A few P′-*f* traces during the eclipse are redrawn in Fig. 10. It is easily seen that though the structure of the F_2 layer near the region of maximum electron density did not change much, the P′-*f* traces at the junction of F_1 and F_2 showed remarkable changes during the eclipse. The variation of virtual heights of reflection of a few fixed frequencies are shown in Fig. 11. Virtual heights of reflections of 5 Mc./s. and of 11 Mc./s. waves did not vary much during the eclipse while those of intermediate frequencies showed a maximum at about 13 hours. The height of reflection of the 6 Mc./s. wave showed the

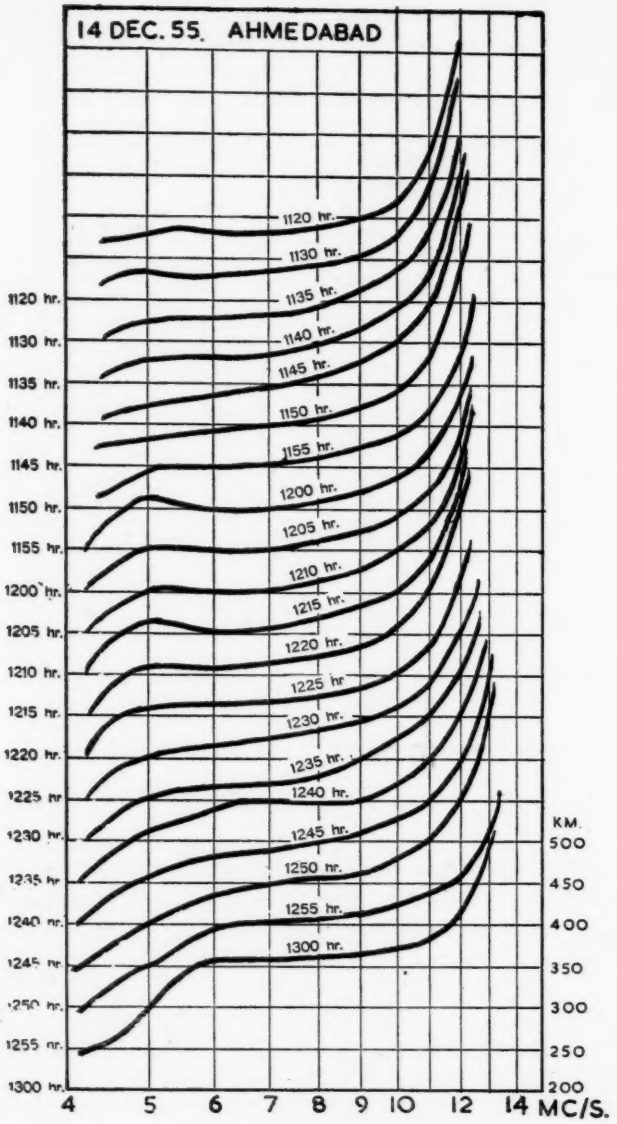

FIG. 10. A few redrawn P′-*f* records obtained on the eclipse day.

maximum change, which was probably at or about the junction of F_1 and F_2 layers.

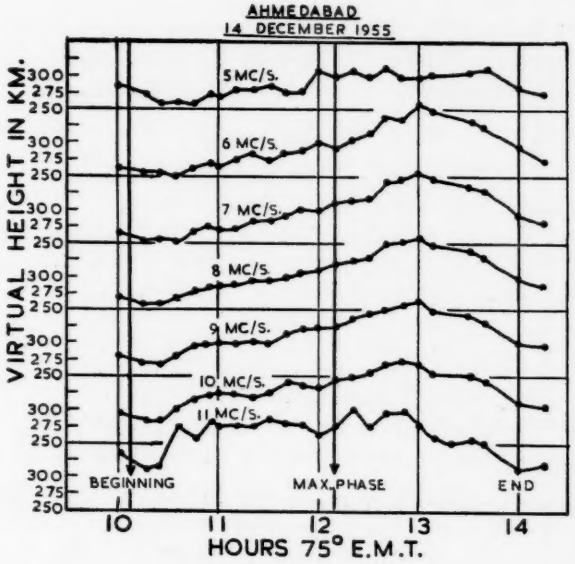

FIG. 11. The variation of the virtual height of reflection for a few fixed frequencies on the eclipse day.

Es layer.—There was no change in the sporadic E layer which could be attributed to the eclipse.

CONCLUSION

The behaviour of E layer during the eclipse was roughly consistent with that of Chapman layer with a recombination coefficient of about $0{\cdot}8 \times 10^{-8}$ cm.^{3}-sec.$^{-1}$

There was no clear effect of the eclipse on the E_1 and E_2 layers; the critical frequencies were lower on the eclipse day.

F_1 layer ionisation decreased during the eclipse but the variation was irregular.

The eclipse caused a fall in the rate of increase of f_0F_2. There was indication of the formation of $F_{1\frac{1}{2}}$ during the later part of the eclipse.

Es was not affected by the eclipse.

ACKNOWLEDGEMENTS

The work described is a part of the studies of the ionosphere during solar eclipse undertaken by the author in this laboratory. The author is greatly indebted to Professor K. R. Ramanathan for his valuable guidance and encouragement. The Council of Scientific and Industrial Research (India) is supporting the Ionospheric Station with financial assistance.

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STUDIES IN THE FORMATION OF HETEROCYCLIC RINGS CONTAINING NITROGEN

Part IV. The Position of Chloro Group in the 1 : 2-Disubstituted Benziminazole from 4-Chloro-*o*-Phenylenediamine and Benzaldehyde

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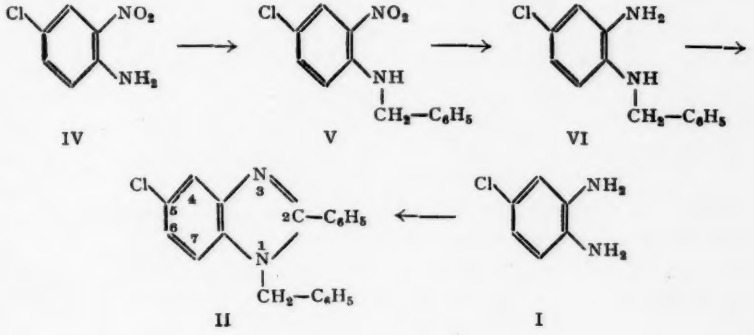
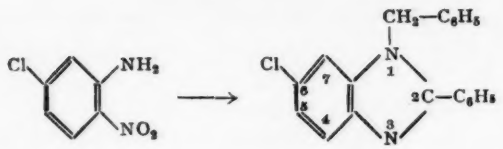
BY the condensation of 4-chloro-*o*-phenylenediamine (I) with more than three molar proportions of benzaldehyde in the absence of any solvent at 150–70°, Fischer and Limmer[1] reported the formation of N : N′-dibenzylidene-4-chloro-*o*-phenylenediamine. They stated further that this dianil, by heating above its melting point, or by boiling in acids, was transformed into the corresponding benziminazole, '*p*-chloro-*ω*-phenyl-N-benzyl benziminazole'. Evidently, the position of the chloro group (5 or 6 position) in this benziminazole has been left unsolved.

The diamine is now condensed with two moles of benzaldehyde following the modified Hinsberg's procedure,[2, 3] when the 1 : 2-disubstituted benziminazole, 2-substituted benziminazole, and a benzodiazepine derivative have been isolated. The 1 : 2-disubstituted benziminazole obtained by us does not agree in its melting point and other properties with that reported by Fischer and Limmer. The product may be either 1-benzyl-2-phenyl-5-chloro benziminazole (II), or 1-benzyl-2-phenyl-6-chloro benziminazole (III). With a view to establishing the structure of this compound, syntheses of the two benziminazoles (II) and (III) have been undertaken adopting a scheme similar to that made use of in the syntheses of the corresponding methyl benziminazoles.[4]





VII III

Starting from 4-chloro-2-nitro aniline (IV), the synthesis of 1-benzyl-2-phenyl-5-chloro benziminazole (II) has been achieved as in the methyl series, through the intermediates, N-benzyl-4-chloro-2-nitro aniline (V), and N^1-benzyl-4-chloro-*o*-phenylenediamine (VI). Similarly, the 6-chloro isomer (III) has been synthesised from 5-chloro-2-nitro aniline (VII) through the corresponding benzyl derivative and diamine.

The 1 : 2-disubstituted benziminazole obtained from benzaldehyde condensation has been found to be identical with 1-benzyl-2-phenyl-5-chloro-benziminazole (II). It may be expected that in all the 1 : 2-disubstituted benziminazoles formed from 4-chloro-*o*-phenylene-diamine and aromatic aldehydes, the chloro group will be in position 5.

EXPERIMENTAL

All m.p.'s are uncorrected. The micro-analyses were carried out by one of the authors (C. V. R.). The experimental procedures are dealt with in a very brief manner, since the various details are exactly similar to those given for methyl series.

I. Condensation of 4-chloro-o-penylenediamine with benzaldehyde

Condensation of 4-chloro-*o*-phenylenediamine (3·6 g.) with benzaldehyde (5·3 g.) in glacial acetic acid at room temperature for a period of one hour yielded 2 : 3 : 4-triphenyl-7-(or 8)-chloro benzodiazepine (0·65 g.), 1 : 2-disubstituted benziminazole (6·5 g.), and 2-phenyl-5-(or 6)-chloro benziminazole (0·7 g.). The diazepine derivative crystallised from alcohol in rectangular rods, m.p. 125° (Found: C, 79·2; H, 5·3; N, 7·4; $C_{27}H_{19}N_2Cl$ requires C, 79·7; H, 4·7; N, 6·9%). The crude disubstituted benziminazole was washed with hot dilute alcohol (1 : 1) and recrystallised from petroleum ether and alcohol to yield prismatic rods, m.p. 171° (Found C, 74·8; H, 5·1; N, 8·5; $C_{20}H_{15}N_2Cl$ requires C, 75·3; H, 4·7; N, 8·8%) (*cf.* Fischer and Limmer, white needles from alcohol, volatalising at about 225°). 2-Phenyl-5-(or 6)-chloro benziminazole came out as plates from alcohol, m.p. 210°, and was found to be identical with the product reported in literature.[5-7]

II. Synthesis of 1-*benzyl*-2-*phenyl*-5-*chloro benziminazole*

(*a*) *N-Benzyl*-4-*chloro*-2-*nitro aniline*.—4-Chloro-2-nitro aniline (5·7 g.), prepared by the method of Crepaz,[8] was benzylated with benzyl chloride (4 ml.), fused sodium acetate (3·0 g.), and iodine (0·07 g.) at 120° for twelve hours. The unreacted amine was separated by trituration with concentrated hydrochloric acid and the crude benzyl derivative (5·0 g.) thus obtained crystallised from petroleum ether in orange-red rhombic plates, m.p. 79° (Found: C, 59·9; H, 4·3; N, 11·2; $C_{13}H_{11}N_2O_2Cl$ requires C, 59·4; H, 4·2; N, 10·7%). Feitelson, and co-workers[9] reported the melting point of the compound as 68°.

(*b*) *N*[1]-*Benzyl*-4-*chloro*-o-*phenylenediamine*.—N-Benzyl-4-chloro-2-nitro aniline (1·0 g.), on reduction with zinc and hydrochloric acid in alcoholic medium at 40–50°, yielded crude N[1]-benzyl-4-chloro-*o*-phenylenediamine (0·8 g.) turning brown in air. The base was characterised as its hydrochloride, tiny rectangular rods from ethyl acetate, m.p. 163° (Found: C, 57·6; H, 5·5; N, 10·8; $C_{13}H_{13}N_2Cl.HCl$ requires C, 58·0; H, 5·2; N, 10·4%).

(*c*) 1-*Benzyl*-2-*phenyl*-5-*chloro benziminazole*.—N[1]-Benzyl-4-chloro-*o*-phenylenediamine (0·47 g.) and benzaldehyde (0·21 g.) were condensed together in alcoholic medium containing nitrobenzene (5 ml.), and the crude benziminazole (0·5 g.) was purified by repeated crystallisations from dilute alcohol, petroleum ether and finally from alcohol. The pure 1-benzyl-2-phenyl-5-chloro benziminazole was obtained as prismatic rods from alcohol, m.p. 172° (Found: C, 75·0; H, 4·9; N, 8·7; $C_{20}H_{15}N_2Cl$ requires C, 75·3; H, 4·7; N, 8·8%). The melting point was undepressed by the 1 : 2-disubstituted benziminazole from the condensation of 4-chloro-*o*-phenylenediamine with benzaldehyde.

III. Synthesis of 1-*benzyl*-2-*phenyl*-6-*chloro benziminazole*

(*a*) *N-Benzyl*-5-*chloro*-2-*nitro aniline*.—5-Chloro-2-nitro aniline (5·7 g.), obtained by the hydrolysis of 5-chloro-2-nitro acetanilide[10] using dilute hydrochloric acid (4:1), when benzylated following the procedure used in II (*a*), gave the crude benzyl derivative (5·0 g.). It crystallised from petroleum ether in bright yellow needles, m.p. 101 (Feitelson and co-workers[9]; m.p. 100–101°).

(*b*) *N*[2]-*Benzyl*-4-*chloro*-o-*phenylenediamine*.—Reduction of N-benzyl-5-chloro-2-nitro aniline (1·0 g.) as in II (*b*) resulted in N[2]-benzyl-4-chloro-*o*-phenyelnediamine (0·7 g.), a viscous pale brown oil. Its hydrochloride was

obtained as almost colourless leaflets from ethyl acetate, m.p. 175° (decomp.) (Found: C, 57·5; H, 5·7; N, 10·7; $C_{13}H_{13}N_2Cl \cdot HCl$ requires C, 58·0; H, 5·2; N, 10·4%).

(*c*) 1-*Benzyl*-2-*phenyl*-6-*chloro benziminazole*.—Condensation of N^2-benzyl-4-chloro-*o*-phenylenediamine (0·47 g.) with benzaldehyde (0·21 g.) as in II (*c*) yielded the crude benziminazole (0·4 g.), which on purification came out as bushy needles from alcohol, m.p. 160° (Found: C, 74·7; H, 5·1; N, 9·1; $C_{20}H_{15}N_2Cl$ requires C, 75·3; H, 4·7; N, 8·8%). The melting point was depressed by the 1 : 2-disubstituted benziminazole obtained in I.

SUMMARY

5-Chloro and 6-chloro, 1-benzyl-2-phenyl-benziminazoles have been synthesised starting from 4-chloro-2-nitro aniline and 5-chloro-2-nitro aniline respectively. The 1 : 2-disubstituted benziminazole obtained by the condensation of 4-chloro-*o*-phenylenediamine with benzaldehyde has been found to be identical with the 5-chloro isomer.

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STUDIES IN THE FORMATION OF HETEROCYCLIC RINGS CONTAINING NITROGEN

Part V. The Position of Nitro Group in the 1 : 2-Disubstituted Benziminazole from 4-Nitro-*o*-Phenylenediamine and Benzaldehyde

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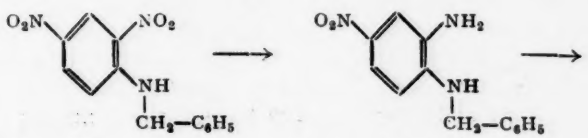
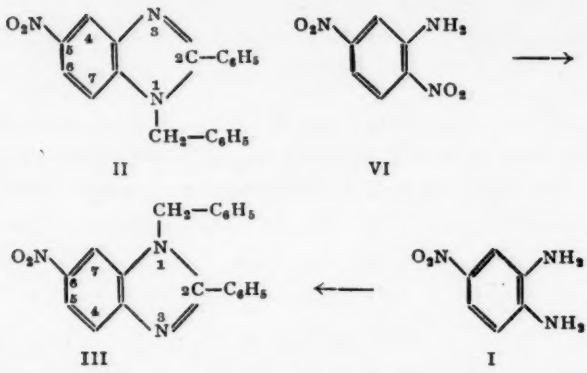
PINNOW AND WISKOTT[1] carried out the condensation of 4-nitro-*o*-phenylenediamine hydrochloride with benzaldehyde, and reported the formation of α-phenyl nitro benziminazole [*i.e.*, 2-phenyl-5-(or 6-)-nitro benziminazole], and N-benyzl-α-phenyl nitro benziminazole (*i.e.*, the 1 : 2-disubstituted benziminazole). They stated that the disubstituted benziminazole can exist in two isomeric forms, 1-benzyl-2-phenyl-5-nitro benziminazole and 1-benzyl-2-phenyl-6-nitro benziminazole. However, they did not succeed in their attempts to fix the position of nitro group in it.

By the condensation of 4-nitro-*o*-phenylenediamine (I) with two moles of benzaldehyde following the modified Hinsberg's procedure,[2] using hot acetic acid due to the very low solubility of the diamine in the cold solvent, both the 2-substituted and 1 : 2-disubstituted benziminazoles could be isolated. Unlike in the condensations of the aldehyde with *o*-phenylenediamine,[2] 4-methyl-*o*-phenylenediamine,[3] and 4-chloro-*o*-phenylenediamine,[4] no benzodiazepine derivative could be isolated in this condensation. The separation of the mono- and disubstituted benziminazoles could be conveniently effected by making use of the selective solubility of the monosubstituted benziminazole in aqueous potash.[1] The compounds thus obtained have been found to be identical with the respective products reported by Pinnow and Wiskott. The position (5 or 6) of the nitro group in the 1 : 2-disubstituted benziminazole has been established, as in the case of methyl[3] and chloro[4] benziminazoles, by synthesising the 5- and 6-nitro benziminazoles (II) and (III) separately by unambiguous methods, and comparing them with the condensation product.



IV V



II VI

III I

1-Benzyl-2-phenyl-5-nitro benziminazole (II) has been synthesised starting from N-benzyl-2: 4-dinitro aniline (IV) in two steps. By the selective reduction of the ortho nitro group in N-benzyl-2: 4-dinitro aniline (IV) making use of ammonium sulphide, N^1-benzyl-4-nitro-*o*-phenylenediamine (V) could be obtained. This diamine (V), on condensation with equimolecular proportion of benzaldehyde in alcoholic nitrobenzene medium, yielded 1-benzyl-2-phenyl-5-nitro benziminazole (II). The synthesis of the 6-nitro benziminazole (III) has been achieved starting from 2: 5-dinitro aniline (VI) in three steps, by benzylation, selective reduction, and benzaldehyde condensation.

The 1: 2-disubstituted benziminazole obtained by the condensation of 4-nitro-*o*-phenylenediamine with benzaldehyde has been found to be identical with 1-benzyl-2-phenyl-6-nitro benziminazole (III). In general, it may be expected that all the 1: 2-disubstituted benziminazoles from 4-nitro-*o*-phenylenediamine and aromatic aldehydes, will have the nitro group in position 6.

EXPERIMENTAL

All m.p.'s are uncorrected. The micro-analyses were carried out by one of the authors (C. V. R.).

I. Condensation of 4-nitro-o-phenylenediamine with benzaldehyde

The diamine (0·51 g.) was dissolved in minimum quantity of almost boiling glacial acetic acid, and benzaldehyde (0·7 g.) was added to it with thorough shaking. The reaction was allowed to proceed for a period of one hour with occasional stirring. The solution was slowly added to excess of crushed ice, and the solid (0·95 g.) that separated was filtered and washed. The crude reaction product thus obtained was triturated with 5% potassium

hydroxide solution. The alkali solution was filtered, and the residue (0·65 g.) was washed with water until free from alkali and dried. The dry substance was purified by recrystallisation, first from alcohol, and then from a mixture of acetone and petroleum ether, yielding the pure disubstituted benziminazole as light yellow prismatic rods, m.p. 187° (*cf.* Pinnow and Wiskott, m.p. 187–88°). The alkaline filtrate was acidified with acetic acid when 2-phenyl-5-(or 6)-nitro benziminazole (0·3 g.) separated out. It was filtered, washed, and on recrystallisation from alcohol, yielded an almost colourless compound, m.p. 203°.[1, 5]

II. Synthesis of 1-*benzyl*-2-*phenyl*-5-*nitro benziminazole*

(*a*) *N*[1]-*Benzyl*-4-*nitro*-o-*phenylenediamine.*—N-Benzyl-2 : 4-dinitro aniline (27 g.), obtained by the method of Cullinane *et al.*,[6] was reduced by means of ammonium sulphide adopting the procedure used for the reduction of 2 : 4-dinitroaniline.[7] The crude reduction product (15 g.), on recrystallisation from alcohol, yielded pure N[1]-benzyl-4-nitro-*o*-phenylenediamine, dark-red rectangular rods, m.p. 148° (Found: C, 63·6; H, 5·2; N, 17·2; $C_{13}H_{13}N_3O_2$ requires C, 64·2; H, 5·4; N, 17·3%).

(*b*) 1-*Benzyl*-2-*phenyl*-5-*nitro benziminazole.*—N[1]-Benzyl-4-nitro-*o*-phenylenediamine (4·0 g.) was dissolved in alcohol (50 ml.), and benzaldehyde (1·8 g.) was added followed by nitrobenzene (25 ml.). The mixture was refluxed on a boiling water-bath for one hour. The solution remaining after the evaporation of alcohol was steam-distilled to remove nitrobenzene, and the residue (4·5 g.) was crystallised repeatedly from alcohol, and finally from a mixture of acetone and petroleum ether. The pure 1-benzyl-2-phenyl-5-nitro benziminazole came out as shining pale yellow rectangular rods, m.p. 160° (Found: C, 73·1; H, 4·4; N, 12·8; $C_{20}H_{15}N_3O_2$ requires C, 73·0; H, 4·6; N, 12·8%). The melting point was depressed by the 1 : 2-disubstituted benziminazole obtained in I.

III. Synthesis of 1-*benzyl*-2-*phenyl*-6-*nitro benziminazole*

(*a*) *N-Benzyl*-2 : 5-*dinitro aniline.*—2 : 5-Dinitro aniline (1·2 g.), obtained from the products of nitration of *m*-nitro acetanilide,[8, 9] fused sodium acetate (0·6 g.), and benzyl chloride (1·6 g.) were taken in a round-bottomed flask fitted with a reflux condenser and a calcium chloride guard tube. A speck of iodine was added, and the mixture was heated at 200° on an oil-bath for a period of twelve hours. The resulting mass was poured into ice-water, stirred well, and the product that separated was filtered. The excess benzyl chloride was removed by pressing the product in folds of filter-paper, and

washing with cold petroleum ether. The remaining solid was washed with dilute sulphuric acid (1 : 1) to remove the unconverted amine, then with water until free from acid, and dried. The crude benzyl derivative (0·6 g.) thus obtained crystallised from benzene in orange-red prisms, m.p. 166° (Found: C, 57·0; H, 4·1; N, 14·9; $C_{13}H_{11}N_3O_4$ requires C, 57·1; H, 4·0; N, 15·4%).

(*b*) *N^2-Benzyl-4-nitro-o-phenylenediamine.*—N-Benzyl-2 : 5-dinitro aniline (0·5 g.) was reduced as in II (*a*), and the reduction product was isolated by diluting the reaction mixture and acidifying it carefully with acetic acid keeping the solution stirred. The crude diamine separated out as a red solid (0·3 g.). Due to the small quantity of the crude diamine available at hand, almost all of it was made use of for the next step. Attempts to prepare a crystalline hydrochloride from 50 mg. of the diamine were unsuccessful.

(*c*) *1-Benzyl-2-phenyl-6-nitro benziminazole.*—N^2-Benzyl-4-nitro-*o*-phenylenediamine (0·24 g.) was condensed with benzaldehyde (0·11 ml.) in alcoholic solution containing nitrobenzene as in II (*b*). The crude product (0·25 g.), on purification from alcohol and then from a mixture of acetone and petroleum ether, yielded pure 6-nitro benziminazole as light yellow prismatic rods, m.p. 187° (Found: C, 72·8; H, 4·9; N, 12·9; $C_{20}H_{15}N_3O_2$ requires C, 73·0; H, 4·6; N, 12·8%). The melting point was undepressed by the 1 : 2-disubstituted benziminazole obtained by the condensation from 4-nitro-*o*-phenylenediamine and benzaldehyde.

SUMMARY

1-Benzyl-2-phenyl-5-nitro benziminazole and 1-benzyl-2-phenyl-6-nitro benziminazole have been synthesised starting from N-benzyl-2 : 4-dinitro aniline and 2 : 5-dinitro aniline respectively. The 1 : 2-disubstituted benziminazole obtained by the condensation of 4-nitro-*o*-phenylenediamine with benzaldehyde has been found to be identical with the 6-nitro benziminazole.

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ANHARMONICITY OF VIBRATION IN MOLECULES

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1. Introduction

Anharmonicity of vibration is responsible for several of the finer features observed in the vibration spectra of molecules, *viz.*, the uneven spacing of the overtone levels of the different normal modes and the splitting of levels that are degenerate in the harmonic oscillator approximation. The spectrum of the vibrational energy levels, when the effect of anharmonic terms in the potential energy of the molecule is taken into account, has been the subject of several investigations, references to which can be had from the well-known books on the subject by Herzberg[1] and by Wilson, Decius and Cross.[2] In a detailed and elaborate piece of work, Nielson[3] has considered the problem for a general molecule taking account of one more complication, *viz.*, the vibration-rotation interaction in the molecule.

In the harmonic oscillator approximation, the normal modes of vibration of the molecule are independent of each other and the energy of the system is the sum of the energies of the $(3n - 6)$ normal modes of the molecule. When anharmonicity is taken into account, product terms of the third and higher powers in the normal co-ordinates are introduced in the potential energy of the system, and as a consequence the normal modes are no longer independent but interact with each other. The standard procedure for obtaining the corrections to the energy levels due to the anharmonic terms is by the perturbation method applied to $N = (3n - 6)$ variables and the results of the theory indicate that the energy levels get altered by the introduction of additional quadratic terms in the vibrational quantum numbers of the normal modes of the molecule. In the present paper, we adopt a different method and follow a procedure well known in the treatment of electronic motion in atoms and molecules, namely the method of the self-consistent field proposed by Hartree. Each normal mode of the molecule is assumed to be moving in the average potential field of vibration of the remaining ones, and the eigenfunctions and energy levels of each of the normal modes are calculated accordingly. Apart from the academic interest of the fact that the Hartree method can be applied to the problems of vibrational motion of the molecule, the procedure deserves attention

since it enables one to regard a molecule as an assembly of anharmonic oscillators and calculate the anharmonicity constants in terms of the force constants of the molecule, and also because it enables one to evaluate a measure of the interaction exerted on each mode by the remaining ones. Thus it is shown in Section 2 that a normal mode of the anti-symmetric species does not interact with the rest even in the first order of approximation. In Section 3, the question of degeneracy has been considered and eigenfunctions and energy values for the case in which one of the modes is doubly degenerate have been evaluated.

2. THE ENERGY LEVELS

We start from the equilibrium configuration of the molecule, that is the configuration in which the forces acting on each atom of the molecule is zero. Referred to this state, the potential energy of the system will not contain any terms linear in the displacements of the atoms. If further we use normal co-ordinates, the potential and kinetic energies will not contain any quadratic cross terms and we can write therefore

$$T = \tfrac{1}{2} \sum_{i=1}^{N} \eta_i^2 \tag{1}$$

$$V = \tfrac{1}{2} \sum_{i=1}^{N} \lambda_i \eta_i^2 + \frac{1}{3!} \sum_i \sum_j \sum_k a_{ijk}\, \eta_i \eta_j \eta_k + \frac{1}{4!} \sum_i \sum_j \sum_k \sum_l \beta_{ijkl}\, \eta_i \eta_j \eta_k \eta_l \tag{2}$$

where $\eta_1, \eta_2, \ldots\ldots \eta_N$ ($N = 3n - 6$ or $3n - 5$ as the case may be) are the normal co-ordinates of the system. We first consider the case in which the system is non-degenerate. The constants $\lambda_1, \lambda_2, \ldots\ldots \lambda_N$ in (2) are then all different.

The wave function $\psi\ (\eta_1 \ldots . \eta_N)$ describing the state of the molecule is given by the solution of the variational principle

$$\delta\,[J] = \delta \int \psi^* H \psi dV = 0 \tag{3}$$

subject to the condition

$$\int \psi^*\, \psi dV = 1 \tag{4}$$

where

$$H = (T + V) \quad \text{and} \quad dV = \prod_{i=1}^{N} d\eta_i.$$

We now try to approximate ψ in terms of the ' one normal co-ordinate ' wave functions $\psi_i(\eta_i)$, each of which depending on one normal co-ordinate only. We set

$$\psi = \psi_{v_1}(\eta_1)\,\psi_{v_2}(\eta_2)\ldots\ldots\ldots\psi_{v_N}(\eta_N) \tag{5}$$

where $v_1, v_2 \ldots\ldots\ldots v_N$ are integral numbers denoting the degree of excitation of the different normal modes, each moving in the field of the rest. The functions $\psi_{v_i}(\eta_i)$ are all assumed to be normalised, and the best possible choice of these which approximate the physical system as closely as possible are obtained as the solution of the variational principle (3). This leads to the following set of differential equations which the ψ's must satisfy.[4]

$$(H_i - \epsilon_i)\,\psi_{v_i} = 0 \tag{6}$$

where

$$H_i = \int \Big(\prod_{k\neq i} \psi_{v_k}^*\Big)\, H \Big(\prod_{k\neq i} \psi_{v_k}\Big) \prod_{k\neq i} d\eta_k \tag{7}$$

ϵ_i is independent of the suffix i and denotes the energy of the whole molecule.

To evaluate the Hamiltonian of the i-th normal mode as well as to determine its eigenfunction, we adopt the procedure of variation-iteration. To a first approximation, we ignore the quartic terms in (2) and substitute for all the wave functions $\psi_{v_k}(\eta_k)\,(k \neq i)$ in (7) the harmonic oscillator eigenfunctions of these normal co-ordinates. The integrals that arise in this process, like $\int \psi^*_{v_k}\,\eta_k^2 \psi_{v_k} d\eta_k$ have been tabulated in Wilson's[2] book and making use of these, we find that equation (6) reduces to

$$\Big\{-\frac{h^2}{8\pi^2}\frac{\partial^2}{\partial \eta_i^2} + (A_{i0}^{(1)} - \epsilon_i^{(1)}) + A_{i1}^{(1)}\eta_i + A_{i2}^{(1)}\,\eta_i^2 + A_{i3}^{(1)}\eta_i^3\Big\}\,\psi_{v_i}(\eta_i) = 0 \tag{8}$$

where

$$A_{i0}^{(1)} = \sum_{l\neq i} (v_l + \tfrac{1}{2})\,h\nu_l;$$

$$A_{i1}^{(1)} = \tfrac{1}{2} \sum_{\substack{m \\ m\neq i}} \frac{a_{mmi}\,(v_m + \frac{1}{2})}{\gamma_m};$$

$$A_{i2}^{(1)} = \frac{\lambda_i}{2};$$

$A_{iii}^{(1)} = \frac{1}{6} a_{iii}$; and

$$\gamma_m = \frac{4\pi^2 \nu_m}{h}. \tag{9}$$

The upper suffix in the above indicates the order of approximation.

Further $\epsilon_i^{(1)} = \int (\Pi \psi^*_{v_i}) \mathrm{H} (\Pi \psi_{v_i}) \Pi d\eta_i$ and by substitution of the harmonic oscillator wave-functions in this we get

$$\epsilon_i^{(1)} = \sum_{l=1}^{N} (v_l + \tfrac{1}{2}) h\nu_l.$$

Hence the eigenvalue of the i-th mode (*i.e.*) $(\epsilon_i^{(1)} - A_0^{(1)})$, is equal to $(v_i + \frac{1}{2})\ h\nu_i$. The first order approximation therfore does not introduce any corrections to the eigenvalues of the different normal modes from their harmonic oscillator values.

From (8) it follows that the Hamiltonian of the oscillator contains an anharmonic cubic term whose coefficient is the same as the coefficient of η_i^3 in the potential energy of the molecule and also a term linear in η_i. The linear term arises out of the process of averaging terms of the type $\eta_i \eta_l^2$ and it gives a measure of the action exerted by the other normal modes on the i-th one. It further suggests that the vibrations of the remaining modes tend to displace the equilibrium position of the i-th one from the place it occupies in the equilibrium configuration of the molecule as a whole.

The coefficient of the linear term is much smaller than the coefficient of the cubic one and their ratio is of the order of $1/\gamma \sim 10^{-16}$. But since the region wherein the displacement of the oscillator has a finite probability is of the order of $\gamma^{-\frac{1}{2}}$, both these terms are of the same order of smallness.

If the i-th mode belongs to an antisymmetric species of vibration of the molecule, all the coefficients of the type a_{mmi} and a_{iii} should be equal to zero. This is because the potential energy, including third and higher order terms, should be invariant under all the symmetry operations of the molecule and there will be at least one operation which will change the sign of a normal co-ordinate falling under an antisymmetric species of the molecule. Thus from (9) it follows that *to a first approximation a normal mode belonging to the antisymmetric species of vibration of the molecule does not interact with the rest and also it suffers no anharmonicity.*

The first order eigenfunctions of (8) may be obtained by the perturbation method. The normalised eigenfunctions are given by

$$\psi_{v_i}^{(1)} = a_i \psi_{v_i}^{(0)} + a_{i-3}^{(0)} \psi_{v_{i-3}}^{(0)} + a_{i-1}^{(0)} \psi_{v_{i-1}}^{(0)} + a_{i+1}^{(0)} \psi_{v_{i+1}}^{(0)} + a_{i+3}^{(0)} \psi_{v_{i+3}}^{(0)} \tag{10}$$

where

$$a_i = 1 - \frac{f_i}{2h^2\nu_i^2(8\gamma_i^3)} + \tfrac{3}{8}\frac{f_i^2}{(8h^2\nu_i^2\gamma_i^3)^2}$$

with

$$f_i = \frac{1}{9}\, v_i(v_i-1)(v_i-2)\,a_i^2 + v_i(3v_ia_i+\beta_i)^2 + (v_i+1)[3(v_i+1)a_i+\beta_i]^2 + \frac{1}{9}(v_i+1)(v_i+2)(v_i+3)\,a_i^2;$$

$$a_{i-3} = \frac{-a_i}{3h\nu_i(8\gamma_i^3)^{\frac{1}{2}}}[v_i(v_i-1)(v_i-2)]^{\frac{1}{2}}a_i;$$

$$a_{i-1} = \frac{-a_i}{h\nu_i(8\gamma_i^3)^{\frac{1}{2}}}\, v_i^{\frac{1}{2}}(3v_ia_i+\beta_i); \tag{11}$$

$$a_{i+1} = \frac{a_i}{h\nu_i(8\gamma_i^3)^{\frac{1}{2}}}(v_i+1)^{\frac{1}{2}}[3(v_i+1)a_i+\beta_i]$$

$$a_{i+3} = \frac{a_i}{3h\nu_i(8\gamma_i^3)^{\frac{1}{2}}}[(v_i+1)(v_i+2)(v_i+3)]^{\frac{1}{2}}a_i$$

and

$$a_i = \frac{-a_{iii}}{6} \quad \text{and} \quad \beta_i = -\gamma_i \sum_{m\neq i}\frac{a_{mmi}(v_m+\frac{1}{2})}{\gamma_m}.$$

The upper suffix in (10) denotes the order of approximation. The zeroth order functions are chosen as the harmonic oscillator eigenfunctions.

To obtain the eigenvalues and eigenfunctions correct to the second order, we substitute the first order eigenfunctions (10) in (7). We now take into account of the quartic terms in the Hamiltonian also. After considerable simplification, the wave function of the ith mode can be written as

$$\left\{-\frac{h^2}{8\pi^2}\frac{\partial^2}{\partial\eta_i^2} + A_{i1}^{(2)}\eta_i + A_{i2}^{(2)}\eta_i^2 + A_{i3}^{(2)}\eta_i^3 + A_{i4}^{(2)}\eta_i^4\right\}\psi_{v_i} = W_i^{(2)}\psi_{v_i} \tag{12}$$

where

$$A_i^{(2)} = \sum_l{}' \frac{a_{lli}(v_l + \frac{1}{2})}{2\gamma_l} + \sum_l{}' \frac{a_{lli}}{16h^2\nu_l^2\gamma_l^4} Q_l$$

$$+ \sum_l{}' \frac{\beta_{llli}}{24\gamma_l^3 h\nu_l} T_l + \sum_{\substack{lm \\ i<m}}{}' \frac{a_{lmi}}{4\gamma_l^2\gamma_m^2 h^2\nu_l\nu_m} R_l R_m$$

$$+ \sum_{lm}{}' \frac{\beta_{llmi}(v_l + \frac{1}{2}) R_m}{4\gamma_m^2\gamma_l h\nu_m};$$

$$A_{i2}^{(2)} = \frac{\lambda_i}{2} + \sum_l{}' \frac{a_{lli}R_l}{4\gamma_l^2 h\nu_l} + \sum_l{}' \frac{\beta_{llii}}{4\gamma_l}(v_l + \tfrac{1}{2});$$

$$A_{i3}^{(2)} = \frac{a_{iii}}{6} + \frac{1}{12}\sum_l{}' \frac{\beta_{liii}}{h\nu_l\gamma_l^2} R_l; \tag{13}$$

$$A_{i4}^{(2)} = \frac{1}{24}\beta_{iiii}$$

and

$$W_i^{(2)} = (v_i + \tfrac{1}{2}) h\nu_i + \frac{K_i}{(8\gamma_i^3) h\nu_i} + \frac{a_{iii}}{24\gamma_i^3 h\nu_i} T_i$$

$$+ \frac{\beta_{iiii}}{32\gamma_i^2}\{2(v_i + \tfrac{1}{2})^2 + \tfrac{1}{2}\}$$

$$+ \sum_l{}' \frac{\beta_{llii}}{4\gamma_l\gamma_i}(v_l + \tfrac{1}{2})(v_i + \tfrac{1}{2})$$

$$+ \left\{\sum_m{}' \frac{a_{iim}}{4\gamma_m^2\gamma_i h\nu_m}(v_i + \tfrac{1}{2}) R_m \right.$$

$$\left. + \sum_m{}' \frac{a_{mmi}}{4\gamma_i^2\gamma_m h\nu_i}(v_m + \tfrac{1}{2}) R_i \right\} \tag{14}$$

In the above the accent indicates that the sum excludes the term l or $m = i$.

The quantities R_l, K_l, T_l and Q_l are given by

$$R_l = 3(2v_l + 1)\,a_l + \beta_l;$$

$$K_l = 30a_l^2\left\{(v_l + \tfrac{1}{2})^2 + \frac{7}{60}\right\} + 12a_l\beta_l(v_l + \tfrac{1}{2}) + \beta_l^2;$$

$$T_l = 30a_l\left\{(v_l + \tfrac{1}{2})^2 + \frac{7}{60}\right\} + 6\beta_l(v_l + \tfrac{1}{2}); \tag{15}$$

$$\begin{aligned} Q_l = K_l &+ \tfrac{1}{3}v_l(v_l - 1)(v_l - 2)(3v_la_l + \beta_l)\,a_l \\ &- v_l(v_l + 1)(3v_la_l + \beta_l)(3v_l + 1a_l + \beta_l) \\ &+ \tfrac{1}{3}(v_l + 1)(v_l + 2)(v_l + 3)[3(v_l + 1)\,a_l + \beta_l]\,a_l \end{aligned}$$

$W_i^{(2)}$ gives the expression for the energy of the ith normal mode.

The energy of the whole molecule is

$$\begin{aligned} \epsilon_i^{(2)} = &\sum_l (v_l + \tfrac{1}{2})\,h\nu_l + \sum_l \frac{K_l}{(8\gamma_l^3)\,h\nu_l} + \sum_l \frac{a_{lll}}{24\gamma_l^3 h\nu_l}T_l \\ &+ \sum_l \frac{\beta_{llll}}{32\gamma_l^2}\{2(v_l + \tfrac{1}{2})^2 + \tfrac{1}{2}\} + \sum_{\substack{lm \\ l\neq m}} \frac{a_{llm}R_m\,(v_l + \tfrac{1}{2})}{4\gamma_m^2\gamma_l h\nu_m} \\ &+ \sum_{\substack{lm \\ l<m}} \frac{\beta_{llmm}}{4\gamma_l\gamma_m}(v_l + \tfrac{1}{2})(v_m + \tfrac{1}{2}) \end{aligned} \tag{16}$$

Remark

We shall define W^{im} by

$$\begin{aligned} W^{im} = \Big\{ &\frac{a_{iim}}{4\gamma_m^2\gamma_i h\nu_m}(v_i + \tfrac{1}{2})\,R_m + \frac{a_{mmi}\,(v_m + \tfrac{1}{2})\,R_i}{4\gamma_i^2\gamma_m h\nu_i} \\ &+ \frac{\beta_{mmii}}{4\gamma_m\gamma_i}(v_m + \tfrac{1}{2})(v_i + \tfrac{1}{2})\Big\} \end{aligned} \tag{17}$$

W^{im} denotes the average interaction energy of the ith and mth modes correct to the second order of approximation. The energy of the whole molecule is related to the energy of the individual modes by means of the relation

$$\epsilon_i^{(2)} = \sum_i W_i^{(2)} - \tfrac{1}{2}\sum_i \sum_m W^{im} \tag{18}$$

3. DEGENERACY

We now consider the case of degeneracy of vibrations. For the sake of preciseness, we consider the case in which one of the modes of vibrations of the molecule is doubly degenerate and the remaining modes are all non-degenerate. The more general cases can be discussed on exactly the same lines. Let us denote the modes that are degenerate with one another by the suffixes (N − 1) and N so that $\nu_{N-1} = \nu_N$. Our problem then is to evaluate the energy values and eigenfunctions of the degenerate mode and to find a measure of its splitting due to anharmonicity.

Let us fix our attention on a state in which the different normal modes of the molecule are excited by $v_1, v_2, \ldots\ldots v_{N-2}$ and v_N quantas respectively. The degeneracy of the overtone level of the doubly degenerate mode is then (v_{N+1}). It is well known that the eigenfunctions for the degenerate mode may be written as

$$\psi_m = N_m e^{(-\gamma_N/2)\rho_N^2} F_{v_N}^{l_N}(\sqrt{\gamma_N}\rho_N)\, e^{\pm i l_N \phi_N} \tag{19}$$

where $F_{v_N}^{l_N}(\sqrt{\gamma_N}\rho_N)$ is a polynomial of degree v_N in $\rho_N\,[=(\eta_{N-1}^2 + \eta_N^2)^{\frac{1}{2}}]$, and l_N is an integer which can assume the values $v_N, v_{N-2}, v_{N-4}, \ldots 1$ or 0 depending on whether v_N is odd or even.

Now the symmetry of an overtone level of degree v_N of a mode which falls under a species Γ of the molecule is given by $(\Gamma)^{v_N}$ and this is in general, a linear sum of the irreducible representations of the point group of the molecule. Thus the wave-functions (19) will transform, under a symmetry operation, like a linear sum of the different irreducible representations of the molecule. Or, alternatively, one can form linear combinations of the above $(v_N + 1)$ wave-functions in such a way that the resulting functions fall exclusively each under any one of the irreducible representations of the symmetry group of the molecule.

Let us suppose that the structure of the level under consideration is given by $\sum_\gamma n^{(\gamma)}\Gamma^{(\gamma)}$ where $\Gamma^{(\gamma)}$ stands for the γth species and $n^{(\gamma)}$ is the number of times this species occurs in the reduced representation of the level. It has been shown by Tisza[5] that only wave-functions which either belong to different irreducible representations or to different matrix representations of the same species can have different energy levels and thus the *maximum* number of components into which the level can be split up by the anharmonic terms is $\Sigma n^{(\gamma)}$.

Let us now subject the set of wave-functions (19) to an orthogonal transformation and obtain a new set of functions $\psi_s^{\gamma a}$ $(s = 1, 2, \ldots . v_{N+1})$ such

that each one of these fall exclusively under one of the irreducible representations of the symmetry group of the molecule. In symbols,

$$\psi_s^{\gamma a} = \sum_{m=1}^{v_{N+1}} C_{sm}^{\gamma a} \psi_m \qquad (s = 1, 2, \ldots . v_{N+1}) \tag{20}$$

where

$$\sum_{m=1}^{(v_{N+1})} (C_{sm}^{\gamma a})^2 = 1 \tag{21}$$

and

$$\sum_{m=1}^{v_{N+1}} C_{sm}^{\gamma a} C_{s'm}^{\gamma' a'} = 0 \qquad (s \neq s')$$

In the above the upper suffix γ denotes the irreducible representation $\Gamma^{(\gamma)}$ under which $\psi_s^{\gamma a}$ falls, and a denotes the matrix representation of the irreducible representation. All functions with different γ and a may therefore be expected to have different energies.

The wave function for the ith mode is now given by

$$(H_i - \epsilon_i)\, \psi_{v_i} = 0 \tag{22}$$

where

$$H_i = \int \left(\prod_{k \neq i} \psi^*_{v_k}\right) H \left(\prod_{k \neq i} \psi_{v_k}\right) \prod_{k \neq i} d\eta_k \tag{22 a}$$

In evaluating the above expression, we may notice that the potential energy of the system does not contain the factors η_{N-1} or η_N individually, but involves these only through the sum of their squares (*i.e.*) through

$$(\eta_{N-1}^2 + \eta_N^2) = \rho_N^2.$$

Thus, we have

$$a_{ijN-1} = a_{ijN} = 0$$

$$(i, j = 1, 2, \ldots . N - 2); \quad a_{N-1\,N-1\,N-1} = a_{NNN} = 0;$$

$$\beta_{ijkN-1} = \beta_{ijkN} = \ldots . = \beta_{iNNN} = 0 \ldots .$$

$$(i, j, k = 1, 2, \ldots . N - 2)$$

and

$$a_{iN-1\,N-1} = a_{iNN}; \quad \beta_{ijN-1\,N-1} = \beta_{ijNN}, \text{ etc.}$$

The first-order energy values and eigenfunctions may be obtained by substituting the harmonic oscillator wave functions for the non-degenerate modes and the function $\psi_S{}^{\gamma a}$ for the degenerate one. We get $\epsilon_i{}^{(1)} = \Sigma (v_i + d_i/2)\, h\nu_i$ where the sum is over all modes with distinct frequencies and d_i denotes the degeneracy of the ith mode. The wave equation is given by the same formulæ (8) and (9) with this difference that the constants $A_{i0}{}^{(1)}$ and $A_{i1}{}^{(1)}$ get modified in this by

$$A_{i0}{}^{(1)} = \sum_j{}' \left(v_j + \frac{d_j}{2}\right) h\nu_j$$

and

$$A_{i1}{}^{(1)} = \tfrac{1}{2} \sum_m{}' \frac{a_{mmi}\left(v_m + \dfrac{d_m}{2}\right)}{\gamma_m} \tag{23}$$

The first order wave equation is therefore still given by (10) with this change that β_i should be defined here by

$$\beta_i = -\gamma_i \Sigma' \frac{a_{mmi}\left(v_m + \dfrac{d_m}{2}\right)}{\gamma_m} \tag{24}$$

For the degenerate mode, the wave equation is given by

$$\left\{-\frac{h^2}{8\pi^2}\left(\frac{\partial^2}{\partial \eta^2{}_{N-1}} + \frac{\partial^2}{\partial \eta_N{}^2}\right) - W_N{}^{(1)} + \frac{\lambda_N}{2}\rho_N{}^2\right\} \psi_{v_N} = 0 \tag{25}$$

where

$$W_N{}^{(1)} = (v_N + 1)\, h\nu_N.$$

We see that in the first order approximation, anharmonicity does not affect the degenerate mode at all.

The Hamiltonian as well as the eigenvalue for the degenerate mode correct to the second order may be obtained by substituting the wave functions given by (10) and (24) in the variational principle (6). One gets

$$\left\{-\frac{h^2}{8\pi^2}\left(\frac{\partial^2}{\partial \eta^2{}_{N-1}} + \frac{\partial^2}{\partial \eta_N{}^2}\right)\right.$$

$$\left. - W_N{}^{(2)} + A_N{}^{(2)}\rho_N{}^2 + A_N{}^{(4)}\rho_N{}^4\right\} \psi_{v_N} = 0 \tag{26}$$

where

$$A_N^{(4)} = \frac{1}{24}\beta_{NNNN};$$

$$A_N^{(2)} = \frac{\lambda_N}{2} + \sum_{l=1}^{N-2} \frac{a_{NNl}}{4\gamma_l^2 h\nu_l} R_l + \sum_{l=1}^{N-2} \frac{\beta_{NNll}(v_l + \frac{1}{2})}{4\gamma_l};$$

$$W_N^{(2)} = (v_N + 1)h\nu_N + \sum_{m=1}^{N-2} \frac{a_{NNm}(v_N + 1)}{4\gamma_m^2 \gamma_N h\nu_m} R_m$$

$$+ \sum_{m} \frac{\beta_{NNmm}}{4\gamma_m \gamma_N}(v_N + 1)(v_m + \tfrac{1}{2})$$

$$+ \frac{\beta_{NNNN}}{16\gamma_N^2}\{(v_N + 1)^2 + \tfrac{1}{3}\} - \frac{\beta_{NNNN}}{48\gamma_N^2}$$

$$\times \{\sum_{m=1}^{v_N+1} (C_{sm}^{\gamma a})^2 l_m^2\} \qquad (27)$$

Since the last term in the above may be expected to be different for functions with different γ and a (*i.e.*) for wave functions falling under different irreducible representations or different matrix representations of the same irreducible representation, each level of the degenerate mode will get split into not more than (Σn^{γ}) sublevels.

The energy of the whole molecule is

$$\epsilon_i^{(2)} = \sum_l \left(v_l + \frac{d_l}{2}\right) h\nu_l + \sum_{l=1}^{N-2} \frac{K_l}{(8\gamma_l^3) h\nu_l}$$

$$+ \sum_{l=1}^{N-2} \frac{a_{lll}}{24\gamma_l^3 h\nu_l} T_l + \sum_{\substack{lm \\ m \neq N}} \frac{a_{llm}\left(v_l + \frac{d_l}{2}\right)}{4\gamma_m^2 \gamma_l h\nu_m} R_m$$

$$+ \sum_{l=1}^{N-2} \frac{\beta_{llll}}{16\gamma_l^2}\{(v_l + \tfrac{1}{2})^2 + \tfrac{1}{4}\}$$

$$+ \sum_{\substack{lm \\ l<m}} \frac{\beta_{llmm}}{4\gamma_l \gamma_m}\left(v_l + \frac{d_l}{2}\right)\left(v_m + \frac{d_m}{2}\right)$$

$$+\frac{\beta_{NNNN}}{16\gamma_N{}^2}\{(v_N+1)^2+\tfrac{1}{3}\}-\frac{\beta_{NNNN}}{48\gamma_N{}^2}$$

$$\times\{\sum_{m=1}^{v_{N+1}}(C_{sm}{}^{\gamma a})^2 l_m{}^2\} \tag{28}$$

Nielson has given explicit expressions for the vibrational energy levels of the molecule. His formula for the energy of the molecule may be written as

$$G(v_1, v_2, \ldots)$$

$$=\sum_i\left(v_i+\frac{d_i}{2}\right)h\nu_i+\sum_{i}\sum_{k>i}^{k} x_{ik}$$

$$\times\left(v_i+\frac{d_i}{2}\right)\left(v_k+\frac{d_k}{2}\right)+\sum_i\sum_{k>i} g_{ik}\, l_i\, l_k \tag{29}$$

In the above, the cross coefficient g_{ik} of the azimuthal quantum numbers l_i and l_k depends on the vibration-rotation interaction of the molecule which is a feature considered in Nielson's work. This explains the absence of the cross terms in the quantum number 'l' in the equation (28). Further, as has been pointed out by Herzberg, the formula (29) gives in general a splitting into fewer levels than what a group theoretical theory would indicate. This is because the wavefunctions used in the evaluation of energy in (29) are the functions (19) and not linear combinations of these falling under different representations of the point group of the molecule. A comparison of (28) with (29) however indicates that the difference is only slight and consists in the replacement of g_{ll} by a coefficient $g_{ll}{}^{\gamma a}$ depending on the symmetry of the state of the sublevel.

For a molecule with several degenerate modes of vibration, the symmetry of a general vibrational level is given by the formula

$$\Gamma=(\Gamma_1)^{v_1}\,\mathbf{X}\,(\Gamma_2)^{v_2}\qquad\qquad\mathbf{X}\,(\Gamma^f)^{v_f} \tag{30}$$

where the '$\mathbf{X}$' denotes the direct product multiplication of groups and $v_1, v_2, \ldots v_f$ are the degrees of excitation of the modes $1, 2, \ldots f$ respectively. Γ is a linear sum of the different irreducible representations of the molecule, and thus by forming linear sums of products of the wavefunctions of the type (19) which fall exclusively under one of the matrix representation of an irreducible representation of the symmetry group of the molecule, one can evaluate the energy levels of the molecule. If one adopts the standard

perturbation method involving N variables, the expected energy levels may be written in the form

$$G^{\gamma a}(v_1 v_2 \ldots v_N) = \sum \left(v_i + \frac{d_i}{2}\right) h\nu_i + \sum_i \sum_{k>i} x_{ik}{}^{\gamma a} \times \left(v_i + \frac{d_i}{2}\right)\left(v_k + \frac{d_k}{2}\right) + \sum_i \sum_{k>i} g_{ik}{}^{\gamma a} l_i l_k \qquad (31)$$

In the above, all coefficients $x_{ik}{}^{\gamma a}$ pertaining to non-degenerate modes will be independent of γ and a, but the coefficients $x_{ik}{}^{\gamma a}$ pertaining to degenerate modes and the coefficients $g_{ik}{}^{\gamma a}$ will, in general, be different for levels of different symmetries.

The author's thanks are due to Professor Sir C. V. Raman for his kind interest in this work.

Summary

The presence of anharmonicity entails the interactions of the normal modes of vibrations, which are independent in the harmonic oscillator approximation. The method of Hartree has been applied to study the mutual interaction of the normal modes, each assumed to be moving in the average potential field of the rest, and to evaluate their wave functions and eigenvalues. It is shown that, to a first order of approximation, normal vibrations belonging to the antisymmetric species do not interact with the rest and suffer no anharmonicity at all. The wave functions and eigenvalues of the different normal modes have been evaluated correct to the second order. The question of degeneracy has been considered and expressions have been given for the energy values of the different sublevels into which an overtone level of a degenerate system may be expected to split up according to group-theoretical considerations.

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HETEROCYCLIC COMPOUNDS

Part XI.* Synthetic Experiments in the Quinazoline Series

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A survey of literature relating to quinazolines revealed that 4-benzyl quinazolines have not received much attention. Fetscher and Bogert[1] attempted the synthesis of 4-veratryl-6: 7-dimethoxy quinazoline, true analogue of papaverine by a method analogous to Pictet papaverine synthesis, but without success. Palit[2] had previously reported failure to cyclise sym-acetyl phenyl urea to 4-methyl-2-quinazolone. The unsuccessful attempts of Bogert and co-workers to cyclise acetyl, phenylacetyl and homoveratroyl derivatives of 3: 4-dimethoxyphenyl urea confirm the failure of this method in this series.

A successful route[3] to 4-alkyl quinazolines is the action of alcoholic ammonia on acyl O-amino ketones under pressure. This method has been modified by Schofield, Theobald and Swain[4] by passing a continuous stream of ammonia for 4–5 hours through molten ammonium acetate containing the requisite ketone, the temperature being maintained at about 165–70°. This communication is a report on the application of this method. The first step is to obtain *o*-acetamido- or *o*-amino phenyl benzyl ketone. Fetscher and Bogert[1] applied three different methods for preparing *o*-amino desoxy veratroin without any success. Goodwin and Lothrop[5] applied the inverse addition of benzyl magnesium chloride to acetanthranil to obtain *o*-amino desoxy benzoin without being able to isolate any tangible product. We first attempted to prepare *o*-amino phenyl benzyl ketone by Hofmann reaction on benzalphthalamide. Hypohalite reaction on the amide (I) gave benzalphthalimide (IV) and benzaldehyde. The imide was recovered unchanged when subjected to Hofmann reaction and smell of benzaldehyde was prominent. The formation of the imide from the amide could be explained by the enolisation of the keto group, replacement of hydroxy by bromine and elimination of hydrogen bromide in the alkaline medium.

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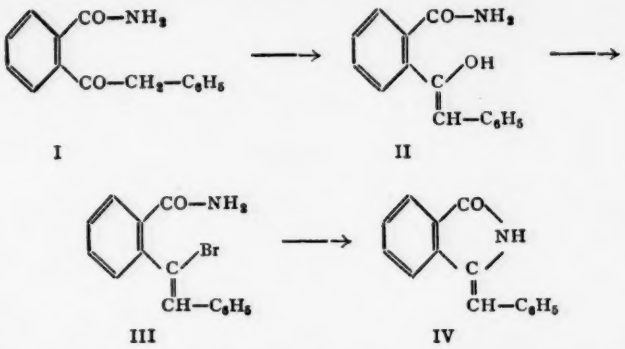
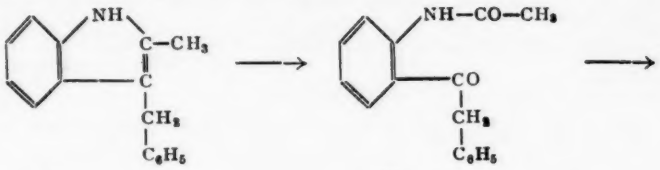


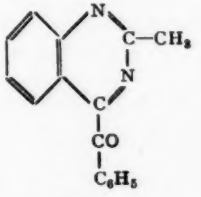
The formation of benzaldehyde in both reactions could possibly be explained by the oxidation of the benzal group by the hypohalite. The resistance of the imide to undergo reaction was unexpected. The application of Friedal-Craft reaction of phenacetyl chloride on *p*-acetanisidide produced only intractable tars. Attention was now turned to the method employed by Hauser and Walker,[6] Bowman,[7] and by Albert and Hampton.[8] *o*-Nitrobenzoyl chloride was condensed with magnesium ethoxy derivative of phenyl diethyl malonate, yielding *o*-nitrobenzoyl-phenyl diethyl malonate. Attempts to acid hydrolyse the product to yield *o*-nitro phenyl benzyl ketone failed. Alkaline conditions cleaved the *o*-nitro benzoyl group to O-nitro benzoic acid. It is relevant to note that Blumer and Sorkin[9] did not succeed to hydrolyse and decarboxylate 3-nitro-6-methyl-benzoyl-*n* butyl diethyl malonate to afford the corresponding ketone. The only product they could isolate was 3-nitro-*o*-toluic acid. Applying Gabriel's method,[10] *o*-phthalimido-benzoyl chloride was condensed with magnesium ethoxy phenyl diethyl malonate and the product hydrolysed without isolation, only phthalimido benzoic acid could be obtained.

Success was achieved in obtaining *o*-acetamido phenyl benzyl ketone in good yield by the ozonolysis of 2-methyl-3-benzyl indole. When this part of the work was completed a paper by Schofield and Okenden[11] appeared on ozonolysis of 2 : 3-disubstituted indoles. When *o*-acetamido phenyl benzyl ketone was treated with gaseous ammonia in molten ammonium acetate, a yellow base of m.p. 142–43° was obtained in satisfactory yield. The compound was expected to be 2-methyl-4-benzyl quinazoline. Analysis of the compound showed it to have the formula $C_{16}H_{12}N_2O$, instead of $C_{16}H_{14}N_2$, pointing to the oxidation of a methylene group at some stage of the reaction. Infra-red spectrum of the compound (see Fig. 8) shows that there is absorption at both 1381 cm.$^{-1}$ and 1667 cm.$^{-1}$ indicating the presence of a C-methyl

group, an $\alpha\beta$-unsaturated ketone and a diaryl ketone. The compound $C_{16}H_{12}N_2O$ is 4-benzoyl-2-methyl-quinazoline.

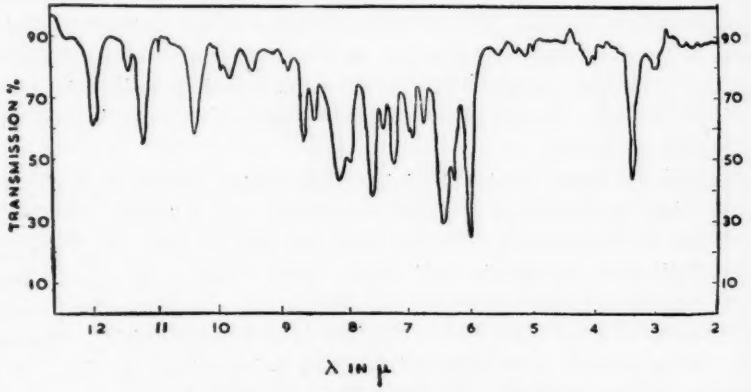


V VI



VII

This is the first reported instance of the formation of a 4-benzoyl quinazoline. Oxidation of a methylene group during synthesis is not without precedent. Quinazoline can be considered to be a quinoline as well as an isoquinoline derivative. The oxidation of a 1-benzyl group in an isoquinoline to the benzoyl group during synthesis has been observed by Haworth, Perkin and Buch[12] and by Gulland and Haworth.[13] A recent publication by



Infra-red Spectrum of 2 methyl-4 benzoyl-quinazoline

Meerwein, Laassh, Mersch and Nentwig[14] reported the preparation of two nuclear substituted 2-phenyl-4-benzyl quinazolines by an entirely different

method. Attempts were made to synthesise 4-benzyl quinazoline by the condensation of benzimid chloride with phenyl acetonitrile in the presence of anhydrous aluminium chloride, but the expected 4-benzyl quinazoline could not be isolated. The problem of preventing the oxidation of the methylene group during the synthesis and the synthesis of substituted 4-benzyl quinazolines are being persued.

Experimental

Hofmann degradation experiments.—Benzalphthalamide and imide were prepared according to the method of Natelson and Gottfried.[15] The amide (5 gm.) dissolved in 10% sodium hydroxide solution (20 ml.) was treated with freshly prepared hypobromite solution at 0° with stirring. After the addition of the hypobromite was complete, the mixture was heated slowly on the water-bath at 80°. Smell of benzaldehyde was noticed. The cooled alkaline solution was extracted with chloroform. The chloroform extract was washed with dilute hydrochloric acid. Basification of the acid extract yielded no product. The chloroform extract was dried and the solvent removed. The resulting solid (m.p. 180–81° from benzene) was benzalphthalimide. When the reaction was carried out with the imide, it was recovered unchanged.

(O-Nitro benzoyl)-phenyl-diethyl-malonate.—Phenyl diethyl malonate was obtained by carbethoxylation of ethyl phenyl acetate with diethyl carbonate according to Gaubert and Smith.[16] An ethereal solution of its magnesium derivative was prepared by standard procedure. A slightly more than equivalent quantity of O-nitro benzoyl chloride in ether was added slowly to the magnesium derivative under stirring, the addition being so regulated that gentle boiling was maintained. After completion of addition the mixture was refluxed for an hour and then left to stand overnight. The magnesium complex was decomposed with cold dilute sulphuric acid and the acid layer extracted with ether. The combined ethereal solution was washed with sodium carbonate (10%), water, dried and ether removed. The resulting oily product solidified on standing in the ice-chest. On crystallisation from ethanol it melted at 103–04°. Found: C, 62·5%, H, 5·1%; N, 3·8%. Calculated for $C_{20}H_{19}NO_7$, C, 62·3%; H, 4·9%; N, 3·6%.

All attempts to hydrolyse the product to the desoxybenzoin failed.

Cyclisation of O-acetamido phenyl benzyl ketone.—O-Acetamido phenyl benzyl ketone was obtained by ozonolysis of 2-methyl-3-benzyl-indole. The ketone (5 gm.) and 50 gm. of dry ammonium acetate were taken in a 300 ml. R.B.-flask and slowly heated to 165° by immersion in an oil-bath, in an

atmosphere of ammonia. A continuous stream of ammonia was passed through the melt for 4 hours. It was then cooled, taken up in water and the aqueous solution left in the ice-chest. A small quantity of a solid separated after some time. The mixture was repeatedly extracted with ethyl acetate and the extract washed with dilute acid. The acid extract was basified with cold, dilute ammonia and then repeatedly extracted with ethyl acetate. After drying over anhydrous magnesium sulphate, ethyl acetate was removed under reduced pressure affording an oil which solidified on standing in the ice-chest. Crystallised from light petrol small yellow shining crystals of m.p. 138–39° were obtained. Found: (1) C, 77·56%; H, 4·95%; N, 11·2%. (2) C, 77·64%; H, 4·85%; N, 11·4%. Calculated for $C_{16}H_{12}N_2O$, C, 77·41%; H, 4·85%; N, 11·2%.

The presence of the keto-group was confirmed by infra-red spectrum.

ACKNOWLEDGEMENT

I take this opportunity to express my thanks to Dr. K. N. Menon for suggesting this problem and for guidance during the course of this work. I thank Government of India for a scholarship and Dr. Gurubakh Singh of the National Physical Laboratory for the infra-red spectrum.

SUMMARY

The synthesis of 4-benzoyl-2-methyl quinazoline is reported.

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